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The Isotope Effect and the Ratio Rule

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A perturbation treatment of the isotope effect has been developed which gives the change in the normal coordinates as well as the frequencies of vibration. The ratio rule is obtained from this treatment, and the conditions which are prerequisite to its application are clearly indicated. At present the lack of required experimental data limits the utility of this rule somewhat, and a more useful but generally less accurate form of it has been derived, which depends for its validity upon the ability to construct symmetry coordinates which approximate the corresponding normal coordinates. The application of these equations to experimental data has been illustrated. In particular the modified ratio rule has been tested on the molecules CD_4, CH_3D, CHD_3, $CDCl_3$, CD_3Cl, ND_3, $B^{10}F_3$, C_2D_4, and C_2D_6 and found to give generally good results.

THE shift in the vibrational frequencies resulting from the introduction of isotope atoms into a molecule has been obtained by several authors[1–3] for certain simple molecules. In addition Wilson[4] has briefly indicated a perturbation method of calculating these shifts which may be more generally applied. For some applications, in particular the calculation of the intensity of the Raman lines of isotopic molecules, it is desirable to have available the equations which give the modification of the normal coordinates. None of the above treatments, with the possible exception of the last, is conveniently adaptable to this end.

It is the purpose of this paper to develop a perturbation treatment of the isotope effect with this end in view. As we shall see, the ratio rules are easily obtained from the equation for the frequency shift.

THEORETICAL

The kinetic and potential energies of the non-isotopic molecule may be written in matrix notation as[5]

$$\begin{aligned} 2T^0 &= \dot{\tilde{R}}(G^0)^{-1}\dot{R} = \dot{\tilde{Q}}^0\dot{Q}^0, \\ 2V^0 &= \tilde{R}F^0R = \tilde{Q}^0\Lambda^0Q^0, \end{aligned} \tag{1}$$

where the transformation from symmetry coordinates to normal coordinates given by

$$R = LQ^0 \tag{2}$$

has been made. Here $\tilde{R}$ is the transpose of the symmetry coordinate matrix R, and Λ^0 is a diagonal matrix whose elements are the

$$\lambda^0{}_i = 4\pi^2\nu^0{}_i{}^2.$$

[1] E. O. Salant and J. E. Rosenthal, Phys. Rev. **42**, 812, 818 (1932).
[2] A. Adel, Phys Rev. **45**, 56 (1934), **46**, 222 (1934).
[3] J. E. Rosenthal, Phys. Rev. **45**, 426, 538 (1934), **46**, 730 (1934), **49**, 535 (1936).
[4] E. B. Wilson, Jr., Phys. Rev. **45**, 427 (1934).
[5] E. B. Wilson, Jr., J. Chem. Phys. **7**, 1047 (1939), **9**, 76 (1941).

The fundamental frequencies of vibration are obtained from the roots (the λ^0_i) of the secular equation

$$|G^0F^0-E\lambda^0|=0, \tag{3}$$

λ^0 being a scalar factor of the unit matrix E. The normal coordinate for the jth frequency, except for a constant factor, may be obtained from the adjoint $A(\lambda^0_j)$ of the matrix $(G^0F^0-E\lambda^0_j)$. Thus

$$A(\lambda^0_j)=k_j\kappa_j, \tag{4}$$

where κ_j is a row matrix whose elements κ_{jk} are proportional to the $L^{-1}{}_{jk}$ and k_j is a column matrix whose elements k_{kj} are proportional to the L_{kj}.[6] Actually any non-zero row (column) of $A(\lambda^0_j)$ is proportional to $\kappa_j(k_j)$, and no distinction is made between them. The adjoint may be obtained in the usual fashion from the minors of the determinant $|G^0F^0-E\lambda^0_j|$ or it may be evaluated as indicated elsewhere.[7] Normalization of κ_{jk} gives

$$L^{-1}{}_{jk}=\kappa_{jk}/\{\textstyle\sum_{mn}\kappa_{jm}\kappa_{jn}G^0{}_{mn}\}^{\frac{1}{2}}. \tag{5}$$

When the introduction of the isotope results in no change in the symmetry, the symmetry coordinates of the ordinary molecule may be used for the isotopic molecule with maximum factorization of the secular equation. However, if the symmetry is lowered, the non-isotopic coordinates generally will produce something less than maximum factorization with all the attendant difficulties.

One notes that every symmetry operation of the isotopic molecule is also a symmetry operation of the non-isotopic molecule; consequently they form a sub-group of the point group of the ordinary molecule. It is thus possible to form a set of symmetry coordinates which *simultaneously* reduces *both* groups—i.e., which are symmetry coordinates for both the isotopic and the ordinary molecules. Such a set of coordinates solves the problem of maximum factorization of the secular equation for the isotopic molecule while using the non-isotopic symmetry coordinates—a requisite for perturbation methods. It is very desirable to obtain explicit expressions for all shifts and this requires the avoidance of the necessity to use the usual methods for handling degeneracy insofar as possible. This is also accomplished by the use of the above coordinates.

Equation (1) is to be considered formed with such coordinates; their use for the isotopic molecule gives

$$2T=\dot{\tilde{R}}G^{-1}\dot{R}=\dot{\tilde{Q}}^0\tilde{L}G^{-1}L\dot{Q}^0 \tag{6}$$

and

$$2V=\tilde{R}F^0R=\tilde{Q}^0\Lambda^0Q^0,$$

the transformation to the normal coordinates of the ordinary molecule, Eq. (2), having been made. Introduction of the normal coordinates for the isotopic molecule, which are related to those of the ordinary molecule by

$$Q^0=BQ \tag{7}$$

results in

$$2T=\dot{\tilde{Q}}\tilde{B}\tilde{L}G^{-1}LB\dot{Q}=\dot{\tilde{Q}}\dot{Q},$$

and (8)

$$2V=\tilde{Q}\tilde{B}\Lambda^0BQ=\tilde{Q}\Lambda Q;$$

and it follows that

$$(L^{-1}G\tilde{L}^{-1})\Lambda^0B=B\Lambda, \tag{9}$$

with Λ a diagonal matrix whose elements are the λ_i. For the set of equations given by (9) to have a non-trivial solution, it is necessary that

$$|(L^{-1}G\tilde{L}^{-1})\Lambda^0-E\lambda|=0, \tag{10}$$

the roots of which are the frequencies of vibration. The transformation B can be obtained from equations analogous to (4) and (5).

This is an exact solution, but it is doubtful whether this procedure is more advantageous than the straightforward method used on the ordinary molecule, unless of course the $L^{-1}{}_{jk}$ are already available or must be obtained in any event.

Of primary importance is the case where Q^0 may be taken as a reasonable approximation to the normal coordinates of the isotopic molecule.[8] Under such conditions $(L^{-1}G\tilde{L}^{-1})$ approximates the unit matrix and perturbation technique may

[6] R. A. Frazer, W. J. Duncan, and A. R. Collar, *Elementary Matrices* (Cambridge University Press, Cambridge, 1938), p. 65.

[7] R. A. Frazer, W. J. Duncan, and A. R. Collar, *Elementary Matrices* (Cambridge University Press, Cambridge, 1938) p. 73.

[8] W. F. Edgell, J. Chem. Phys. **13**, 306 (1945).

be used. Writing

$$L^{-1}G\tilde{L}^{-1}=E+J, \quad B=B^0+B'+B''+, \qquad \Lambda=\Lambda^0+\Lambda'+\Lambda''+, \tag{11}$$

and substituting into Eq. (9) yields

zero order:

$$B^0\Lambda^0=\Lambda^0B^0,$$

first order:

$$B^0\Lambda'+B'\Lambda^0=\Lambda^0B'+J\Lambda^0B^0, \tag{12}$$

second order:

$$B^0\Lambda''+B'\Lambda'+B''\Lambda^0=\Lambda^0B''+J\Lambda^0B'.$$

To normalize B, one notes that

$$B\tilde{B}=L^{-1}G\tilde{L}^{-1},$$

which when combined with Eq. (11), gives

zero order:

$$B^0\tilde{B}^0=E,$$

first order:

$$B^0\tilde{B}'+B'\tilde{B}^0=J, \tag{13}$$

second order:

$$B^0\tilde{B}''+B'\tilde{B}'+B''\tilde{B}^0=0.$$

The solution of these equations, correct to the second order, is

$$\lambda_i/\lambda^0{}_i=1+J_{ii}+\sum'_k J^2{}_{ik}\lambda^0{}_k/(\lambda^0{}_i-\lambda^0{}_k)+, \tag{14}$$

with

$$B_{ii}=1+J_{ii}/2-J^2{}_{ii}/8 -\sum'_k\{J_{ik}\lambda^0{}_k/(\lambda^0{}_k-\lambda^0{}_i)\}^2/2+, \tag{15}$$

and

$$B_{ij}=\frac{\lambda^0{}_j}{\lambda^0{}_j-\lambda^0{}_i}\{J_{ij}-J_{ij}J_{jj}(\lambda^0{}_j+\lambda^0{}_i)/2(\lambda^0{}_j-\lambda^0{}_i) +\sum'_k J_{ik}J_{kj}\lambda^0{}_k/(\lambda^0{}_j-\lambda^0{}_k)+\}. \tag{16}$$

Since one is concerned here with finite matrices, the treatment always converges,[9] although naturally the better the Q^0 approximates the true normal coordinates of the isotopic molecule the fewer terms will be required to obtain a given accuracy.

[9] A. H. Wilson, Proc. Roy. Soc. **A122**, 589 (1929), **A124**, 176 (1929).

The Ratio Rule

Recently Noether[10] has found that the results of his studies on the isotopic methyl halides could be expressed very well by the following empirical *ratio rule*:

$$\frac{\nu_i(CD_3Cl)}{\nu_i(CH_3Cl)}=\frac{\nu_i(CD_3Br)}{\nu_i(CH_3Br)}. \tag{17}$$

Until recently[8] there was no theoretical justification for this rule although it was shown that it could be extended to other pairs of isotopic molecules of similar symmetry.

It is apparent that (14) is the fundamentally basic equation of the ratio rule. To the first order it may be written as

$$\lambda_i/\lambda^0{}_i=1+[L^{-1}(G-G^0)\tilde{L}^{-1}]_{ii}. \tag{18}$$

If two pairs of molecules satisfy the following conditions: (*a*) each pair gives rise to equal elements of $(G-G^0)$, and (*b*) each non-isotopic molecule has (essentially) the same normal coordinates, it follows that $\lambda_i/\lambda^0{}_i$ has the same value for each pair. Taking the square root gives

$$(\nu_i/\nu^0{}_i)_A=(\nu_i/\nu^0{}_i)_B. \tag{19}$$

This is the ratio rule. Whenever these conditions are fulfilled, as in the molecules of Eq. (17), excellent results may be expected.[11] Clearly one is not limited to considering only pairs of molecules of the same symmetry, for many others will satisfy (or approximate) the prerequisites, for example CH_3Cl—CH_2DCl and CH_3Br—CH_2DBr.

Because the ratio rule deals with individual frequencies, more detailed information is obtained from it than from the well-known product rule.[5,12–14] Unfortunately, however, its application requires experimental data not generally available at present.

In view of this fact it seems worth while to investigate to what extent Eq. (14) can be made to yield simplified results. This equation may be

[10] H. F. Noether, J. Chem. Phys. **11**, 97 (1943).
[11] See Table I of reference 10 or Table IV of this paper.
[12] E. Teller, quoted in C. K. Ingold *et al.* J. Chem. Soc., London, 971 (1936).
[13] O. Redlich, Zeits. f. physik. Chemie **B28**, 371 (1935).
[14] Of course Eq. (19) may also be applied to cases where the requisite conditions are less exactly satisfied (see reference 10) with a corresponding loss in accuracy.

TABLE I. Force constants in $CHCl_3$ and $CDCl_3$ (see reference 17).

K_{Cl}	3.54[a]	k_{ClCl}	0.39
K_H	4.98	$k_{Cl\alpha}'$	0.23
K_α	0.207	$k_{Cl\alpha}$	−0.29
K_β	0.48		

[a] The units are 10^5 dynes/cm.

TABLE II. Comparison between calculated and observed frequencies in $CHCl_3$ and $CDCl_3$ (see reference 17).

	Vibration	Calc.	Obs.	Dev.
$CHCl_3$	A_1 ν_1	668 cm^{-1}	669 cm^{-1}	−0.1%
	ν_2	3020	3019	0.03
	ν_3	366	366	0.0
	E ν_4	1215	1215	0.0
	ν_5	258	262	−1.5
	ν_6	763	761	0.2
$CDCl_3$	A_1 ν_1	648	651	−0.4
	ν_2	2226	2256	−1.3
	ν_3	363	367	−1.0
	E ν_4	917	908	1.0
	ν_5	256	262	−2.1
	ν_6	729	738	−1.1

written, to the first order, as

$$\lambda_i/\lambda^0{}_i=(L^{-1}G\tilde{L}^{-1})_{ii}. \quad (20)$$

On using Eq. (5) one obtains

$$\lambda_i/\lambda^0{}_i=\sum_{kj}\kappa_{ik}\kappa_{ij}G_{kj}/\sum_{mn}\kappa_{im}\kappa_{in}G^0{}_{mn}. \quad (21)$$

If the ith normal coordinate is closely approximated by the ith symmetry coordinate, the principal terms of (21) involve $\kappa^2{}_{ii}$, and one may write that

$$\lambda_i/\lambda^0{}_i\approx G_{ii}/G^0{}_{ii}. \quad (22)$$

This simple relationship does not require generally unavailable experimental data from similar molecules, hence it is less restricted in use. But it is necessary to provide a symmetry coordinate in advance which is reasonably close to each normal coordinate!

Approximate Degeneracy

When the isotopic substitution results in a molecule of lower symmetry, it sometimes happens that several frequencies of the same symmetry have zero-order values that are nearly equal.[15] An example of this occurs in the A_1 vibrations of CH_3D, where the C—H and C—D vibrations have as their zero-order values the A_1 and T_2 C—H vibrations of CH_4. In this event Eq. (14) can become awkward in use, and it will be advantageous to diagonalize this portion of the matrix by the usual degenerate perturbation technique. Thus when two frequencies are involved,

$$\begin{vmatrix}(1+J_{11})\lambda^0{}_1-\lambda & J_{12}\lambda^0{}_2\\ J_{21}\lambda^0{}_1 & (1+J_{22})\lambda^0{}_2-\lambda\end{vmatrix}=0. \quad (23)$$

If both normal coordinates are closely approximated by symmetry coordinates, this may be written as

$$\begin{vmatrix}G_{11}\lambda^0{}_1/G^0{}_{11}-\lambda & G_{12}\lambda^0{}_2/(G^0{}_{11}G^0{}_{22})^{\frac{1}{2}}\\ G_{12}\lambda^0{}_1/(G^0{}_{11}G^0{}_{22})^{\frac{1}{2}} & G_{22}\lambda^0{}_2/G^0{}_{22}-\lambda\end{vmatrix}=0. \quad (24)$$

COMPARISON WITH EXPERIMENTAL DATA

The calculation of the vibrational frequencies of $CDCl_3$ is taken as an example of the application of the perturbation equations. The symmetry coordinates chosen are:

A_1: $R_1=(r_1+r_2+r_3)/3^{\frac{1}{2}}$,

$R_2=r_4$,

$R_3=(\alpha_1+\alpha_2+\alpha_3-\beta_{12}-\beta_{23}-\beta_{13})/6^{\frac{1}{2}}$.

TABLE III. The vibrational frequencies of $CDCl_3$ by Eq. (14).

Vibration	$CHCl_3$[a]	1st Order	2nd Order	Eq. (10)[a]
A_1 ν_1	669 cm^{-1}	658 cm^{-1}	653 cm^{-1}	648 cm^{-1}
ν_2	3020	2223	2225	2226
ν_3	366	365	364	363
E ν_4	1215	897	903	917
ν_5	258	257	256	256
ν_6	763	753	745	729

[a] The approximate calculation is compared here with the exact calculation.

TABLE IV. The vibrational frequencies of CD_3Cl by Eq. (19).

Vibration	CH_3Cl	CH_2Br	CD_2Br	CD_3Cl(calc.)	CD_3Cl(obs.)	Dev.
A_1 ν_1	2924[a] cm^{-1}	2916[a] cm^{-1}	2120[a] cm^{-1}	2126 cm^{-1}	2133[a] cm^{-1}	−0.3%
ν_2	732	610	577	692	695	−0.4
ν_3	1355	1305	987	1025	1029	−0.4
E ν_4	1020	957	717	764	775	−1.4
ν_5	1460	1450	1053	1060	1058	+0.2
ν_6	3047	3061	2294	2283	2287	−0.2

[a] The average of the resonating frequencies.

[15] As pointed out in the text, the symmetry coordinates used avoid any actual degeneracy.

$$E: \quad R_{4a}=(\alpha_1-\alpha_2)/2^{\frac{1}{2}},$$
$$R_{5a}=(\beta_{23}-\beta_{13})/2^{\frac{1}{2}},$$
$$R_{6a}=(r_1-r_2)/2^{\frac{1}{2}},$$
$$R_{4b}=(\alpha_1+\alpha_2-2\alpha_3)/6^{\frac{1}{2}},$$
$$R_{5b}=(\beta_{23}+\beta_{13}-2\beta_{12})/6^{\frac{1}{2}},$$
$$R_{6b}=(r_1+r_2-2r_3)/6^{\frac{1}{2}};$$

where r_1, r_2, and r_3 denote changes in the C—Cl distances, r_4 the C—H or C—D distance, α_1, α_2, and α_3 the H—C—Cl or D—C—Cl angles, and β_{12}, β_{23}, and β_{13} the Cl—C—Cl angles.[16] The assumed potential energy expression is

$$2V=K_{Cl}(r_1^2+r_2^2+r_3^2)+K_H r_4^2$$
$$+K_\alpha l_x^2(\alpha_1^2+\alpha_2^2+\alpha_3^2)$$
$$+K_\beta l_x^2(\beta_{12}^2+\beta_{13}^2+\beta_{23}^2)$$
$$+2k_{ClCl}(r_1r_2+r_2r_3+r_3r_1)$$
$$+2k_{Cl\alpha}l_x\{\alpha_1(r_2+r_3)+\alpha_2(r_1+r_3)$$
$$+\alpha_3(r_1+r_2)\}+2k'_{Cl\alpha}l_x(r_1\alpha_1+r_2\alpha_2+r_3\alpha_3),$$

where l_x, the C—Cl distance (1.77A), has been used to give dimensional uniformity. The values taken for the force constants are those previously obtained[17] and are found in Table I.[18] These lead to the following normal coordinates for $CHCl_3$:[19]

$$A_1: \quad Q_1=3.11954\,R_1+0.24769\,R_2+0.53531\,l_xR_3,$$
$$Q_2=-0.03054\,R_1+0.96105\,R_2$$
$$-0.01013\,l_xR_3,$$
$$Q_3=-4.71325\,R_1+0.12096\,R_2$$
$$+1.84399\,l_xR_3;$$
$$E: \quad Q_4=0.48289\,l_xR_4+0.04761\,l_xR_5+1.41678\,R_7,$$
$$Q_5=0.05781\,l_xR_4+2.87372\,l_xR_5-3.74619\,R_7,$$
$$Q_6=-0.11502\,l_xR_4+0.67090\,l_xR_5$$
$$+1.57626\,R_7.$$

The calculated values (Eq. (10)) are compared with the observed values in Table II, while the results of the perturbation treatment are compared with the more accurately calculated values in Table III. The outcome is gratifying.

Noether[10] has considered the application of the

TABLE V. The vibrational frequencies of CD_4 by Eq. (22).

Vibration	CH_4	$(G_{ii}/G^0_{ii})^{\frac{1}{2}}$	CD_4 (calc.)	CD_4 (obs.)[a]	Dev.
A_1 ν_1	2915 cm^{-1}	0.707	2060 cm^{-1}	2085 cm^{-1}	−1.2%
E ν_2	1520	0.707	1073	(1054)[b]	+1.8
T_2 ν_3	3020	0.742	2240	2258	−0.8
ν_4	1306	0.769	1004	996	+0.8

[a] The experimental data are taken from the compilations of: Ta You Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (China Science Corporation, Shanghai, 1939); and G. Herzberg, *Infra-red and Raman Spectra of Polyatomic Molecules* (Van Nostrand Company, Inc., New York, 1945).
[b] Obtained from the overtone $2\nu_2=2108$ cm^{-1}. See reference *a*, G. Herzberg, p. 307.

TABLE VI. The vibrational frequencies of $CDCl_3$ by Eq. (22).

Vibration	$CHCl_3$	$(G_{ii}/G^0_{ii})^{\frac{1}{2}}$	$CDCl_3$ (calc.)	$CDCl_3$ (obs.)	Dev.
A_1 ν_1	669 cm^{-1}	1	669 cm^{-1}	651 cm^{-1}	+2.8%
ν_2	3019	0.7340	2216	2256	−1.8
ν_3	366	1	366	367	−0.3
E ν_4	1215	0.7465	908	908	0
ν_5	262	1	262	262	0
ν_6	761	1	761	738	+3.1

[16] These coordinates yield somewhat different G matrices than those given by Wilson (reference 5).

TABLE VII. The vibrational frequencies of CD_3Cl by Eq. (22).[a]

Vibration	CH_3Cl	$(G_{ii}/G^0_{ii})^{\frac{1}{2}}$	CD_3Cl (calc.)	CD_3Cl (obs.)	Dev.
A_1 ν_1	2924[b] cm^{-1}	0.7194	2104 cm^{-1}	2133[b] cm^{-1}	−1.4%
ν_2	732	1	732	695	+5.3
ν_3	1355	0.7692	1042	1029	+1.3
E ν_4	1020	0.7519	767	775	−1.0
ν_5	1460	0.7407	1081	1058	+2.1
ν_6	3047	0.7463	2274	2287	−0.6

[a] See similar calculation of Noether, reference 10.
[b] The average of the resonating frequencies.

TABLE VIII. The vibrational frequencies of ND_3 by Eq. (22).

Vibration	NH_3	$(G_{ii}/G^0_{ii})^{\frac{1}{2}}$	ND_3 (calc.)	ND_3 (obs.)	Dev.
A_1 ν_1	3334 cm^{-1}	0.7183	2395 cm^{-1}	2420 cm^{-1}	−1.0%
ν_2	950[a]	0.7595	722	748	−3.5
E ν_3	(3450)[b]	0.7359	2539	2556	−0.7
ν_4	1628	0.7288	1186	1191	−0.4

[a] The average of the split lines.
[b] G. B. B. M. Sutherland, Phys. Rev. **56**, 836 (1939).

[17] W. F. Edgell, "Studies in Molecular Structure," M.S. Thesis (State University of Iowa, 1941).
[18] It is not claimed that these force constants give the best possible representation of the potential energy to this approximation but only that they reproduce the observed frequencies in $CHCl_3$ and $CDCl_3$ with reasonable accuracy.
[19] The figures given here are those actually used in the calculation, and of course all of them are not significant.

TABLE IX. The vibrational frequencies of $B^{10}F_3$ by Eq. (22).

Vibration	$B^{11}F_3$	$(G_{ii}/G^0_{ii})^{\frac{1}{2}}$	$B^{10}F_3$ (calc.)	$B^{10}F_3$ (obs.)	Dev.
A_1' ν_1	886 cm^{-1}	1	886 cm^{-1}	886 cm^{-1}	0 %
A_2'' ν_2	694	1.018	707	722	−2.1
E' ν_3	1448	1.0355	1499	1501	−0.1
ν_4	440	1.0355	455	440	+3.6

TABLE X. The vibrational frequencies of CHD_3 by Eq. (22) and Eq. (24).

Vibration	CH_4	$(G_{ii}/G^0_{ii})^{\frac{1}{2}}$	CHD_3 (calc.)	CHD_3 (obs.)	Dev.
A_1 ν_1	2915 cm^{-1}	[a]	2103 cm^{-1}	2141 cm^{-1}	−1.8%
ν_2	3020	[a]	2998	3015	−0.6
ν_3	1306	0.769	1003	988	+1.5
E ν_4	(1520)	[a]	1283	1295	−0.9
ν_5	1306	[a]	1034	1046	−1.1
ν_6	3020	0.742	2240	2263	−1.0

[a] Frequency calculated by Eq. (24).

ratio rule, i.e., Eq. (19), in some detail. The prerequisite conditions obtained above make it clear why the rule does not give good results in certain instances. However, when these requirements are fully satisfied, the results are excellent. This is illustrated in Table IV where the frequencies of CD_3Cl are calculated from those of CH_3Cl, CH_3Br, and CD_3Br.[20]

Since the data required to apply Eq. (19) are not generally available at present, Eq. (22) will be investigated in some detail. Of late little effort has been made to obtain the actual form of the fundamental vibrations, i.e., the normal coordinates, and so no ready fund of data exists which may be drawn upon to form *a priori* symmetry coordinates which closely approximate the normal coordinates. In the following no special effort is made to do this, the symmetry coordinates, which are collected in the appendix, being formed in the usual manner from valency type internal coordinates. The results for CD_4, $CDCl_3$, CD_3Cl, ND_3, and $B^{10}F_3$ are good and are found in Tables V–IX. The results for CHD_3 and CDH_3 are found in Tables X and XI. These two molecules have near degeneracies in the zero-order frequencies for both the A_1 and E symmetry types, and Eq. (24) was used to calculate such frequencies, the remainder being obtained from Eq. (22). As can be seen the results are excellent.

One should not conclude from the above examples that the results of the application of Eq. (22) (or Eq. (24)) are uniformly good. Tables XII and XIII contain the outcome for C_2D_4 and C_2D_6. Several calculated frequencies in these molecules agree but poorly with the observed values. This indicates a serious discrepancy between the symmetry coordinates chosen and the actual normal coordinates for these frequencies. Indeed such differences also exist for the molecules listed in Table VI–IX. It is apparent, however, that they are unimportant as long as each normal coordinate in which the motion of the isotopic atoms are prominent is closely approximated by a symmetry coordinate. How this occurs in practice may be seen by comparing the normal coordinates of $CHCl_3$ with Table VI.

In spite of this difficulty, which must introduce some uncertainty, the results obtained as a whole demonstrate the usefulness of Eq. (22).

The results obtained herein, in particular Eqs. (19) and (22), should prove to be valuable additions to the Teller-Redlich product rule.[12,13] Their utility lies in the fact that they deal with individual frequencies.

APPENDIX

CH_4

The symmetry coordinates for CH_4 that were used in the CD_4 calculation were:

$$A_1: \quad R^0_1=(r_1+r_2+r_3+r_4)/2;$$

$$E: \quad R^0_{2a}=(\alpha_{12}-\alpha_{13}+\alpha_{34}-\alpha_{24})/2,$$

$$R^0_{2b}=(\alpha_{12}+\alpha_{13}+\alpha_{34}+\alpha_{24}-2\alpha_{14}-2\alpha_{23})/12^{\frac{1}{2}};$$

TABLE XI. The vibrational frequencies of CDH_3 by Eq. (22) and Eq. (24).

Vibration	CH_4	$(G_{ii}/G^0_{ii})^{\frac{1}{2}}$	CDH_3 (calc.)	CDH_3 (obs.)	Dev.
A_1 ν_1	2915 cm^{-1}	[a]	2950 cm^{-1}	2983 cm^{-1}	−1.1%
ν_2	3020	[a]	2186	2205	−0.9
ν_3	1306	1	1306	1307	−0.1
E ν_4	(1520)		1460	1477	−1.2
ν_5	1306	[a]	1153	1156	−0.3
ν_6	3020	1	3020	3031	−0.4

[a] Frequency calculated by Eq. (24).

[20] The results contained in this table are taken from Table I, of reference 10.

$$T_2:\ R^0_{3a}=(r_1-r_2-r_3+r_4)/2,$$

$$R^0_{3b}=(r_1+r_2-r_3-r_4)/2,$$

$$R^0_{3c}=(r_1-r_2+r_3-r_4)/2,$$

$$R^0_{4a}=(\alpha_{14}-\alpha_{23})/2^{\frac{1}{2}},$$

$$R^0_{4b}=(\alpha_{12}-\alpha_{34})/2^{\frac{1}{2}},$$

$$R^0_{4c}=(\alpha_{13}-\alpha_{24})/2^{\frac{1}{2}},$$

with r_1, etc., and α_{12}, etc., denoting the change in the C—H distances and the H—C—H angles. For the CH_3D and CHD_3 calculations the following coordinates were used:

$$A_1:\ R_1=R^0_1,$$

$$R_2=(R^0_{3a}+R^0_{3b}+R^0_{3c})/3^{\frac{1}{2}},$$

$$R_3=(R^0_{4a}+R^0_{4b}+R^0_{4c})/3^{\frac{1}{2}};$$

$$E:\ R_{4a}=R^0_{2a},$$

$$R_{4b}=R^0_{2b},$$

$$R_{5a}=(R^0_{4b}-R^0_{4c})/2^{\frac{1}{2}},$$

$$R_{5b}=(-2R^0_{4a}+R^0_{4b}+R^0_{4c})/6^{\frac{1}{2}},$$

$$R_{6a}=(R^0_{3b}-R^0_{3c})/2^{\frac{1}{2}},$$

$$R_{6b}=(-2R^0_{3a}+R^0_{3b}+R^0_{3c})/6^{\frac{1}{2}}.$$

These coordinates are symmetry coordinates for both CH_4 and CH_3D (or CHD_3). The G^0 matrix for CH_4 obtained with these coordinates is the same as with the first set.

$CHCl_3$ and CH_3Cl

These coordinates are found in the text.

TABLE XII. The vibrational frequencies of C_2D_4 by Eq. (22).

Vibration	C_2H_4	$(G_{ii}/G^0_{ii})^{\frac{1}{2}}$	C_2D_4 (calc.)	C_2D_4 (obs.)	Dev.
A_{1g} ν_1	3020 cm^{-1}	0.721	2180 cm^{-1}	2252 cm^{-1}	−3.2%
ν_2	1623	1	1623	1515	+7.3
δ_{CH_2}	1341	0.745	1000	981	+1.9
B_{1u} ν_{CH_2}	2988	0.721	2155	2192	−1.7
δ_{CH_2}	1444	0.745	1078	1077	+0.1
B_{2g} ν_{CH_2}	3075[a]	0.745	2290	2306	−0.7
δ_{CH_2}	944	0.845	795	780	+1.9
B_{3u} ν_{CH_2}	3107	0.745	2317	2335	−0.8
δ_{CH_2}	(950)[a]	0.721	685	(678)[a]	+1.0

[a] See reference *a* of Table V, Ta You Wu, p. 267.

TABLE XIII. The vibrational frequencies of C_2D_6 by Eq. (22).

Vibration	C_2H_6	$(G_{ii}/G^0_{ii})^{\frac{1}{2}}$	C_2D_6 (calc.)	C_2D_6 (obs.)	Dev.
A_{1g} ν_1	2927[a] cm^{-1}	0.7166	2098 cm^{-1}	2114[a] cm^{-1}	− 0.8%
ν_2	(1375)[b]	0.7687	1057	1158	− 8.7
ν_3	993	1	993	852	+16.5
A_{2u} ν_5	2954	0.7166	2117	2111	+ 0.3
ν_6	1379	0.7687	1060	1072	− 1.1
E_u ν_7	2994	0.7416	2221	2236	− 0.7
ν_8	1486	0.7354	1093	1102	− 0.8
ν_9	821	0.7119	584	601	− 2.8
E_g ν_{10}	2963	0.7416	2197	2225	− 1.3
ν_{11}	1460	0.7354	1074	1055	+ 1.8
ν_{12}	(1170)[c]	0.7989	935	970	− 3.6

[a] Average of the resonating lines.
[b] From combination band, see reference *a* of Table V, G. Herzberg, p. 345.
[c] Obtained by use of the product rule, see reference *a* of Table V, G. Herzberg, p. 345.

NH_3

For the ND_3 calculation the following symmetry coordinates were used:

$$A_1:\ R_1=(r_1+r_2+r_3)/3^{\frac{1}{2}},$$

$$R_2=(\alpha_{12}+\alpha_{23}+\alpha_{13})/3^{\frac{1}{2}};$$

$$E:\ R_{3a}=(r_1-r_2)/2^{\frac{1}{2}},$$

$$R_{3b}=(r_1+r_2-2r_3)/6^{\frac{1}{2}},$$

$$R_{4a}=(\alpha_{23}-\alpha_{13})/2^{\frac{1}{2}},$$

$$R_{4b}=(\alpha_{23}+\alpha_{13}-2\alpha_{12})/6^{\frac{1}{2}}.$$

r_1, etc., and α_{12}, etc., denote the changes in the N—H distance and the H—N—H angles.

BF_3

The coordinates used were:

$$A_1':\ R_1=(r_1+r_2+r_3)/3^{\frac{1}{2}};$$

$$A_2'':\ R_2=(z_4-z_1-z_2-z_3)/2;$$

$$E':\ R_{3a}=(r_1-r_2)/2^{\frac{1}{2}},$$

$$R_{3b}=(r_1+r_2-2r_3)/6^{\frac{1}{2}},$$

$$R_{4a}=(\alpha_{23}-\alpha_{13})/2^{\frac{1}{2}},$$

$$R_{4b}=(\alpha_{23}+\alpha_{13}-2\alpha_{12})/6^{\frac{1}{2}}.$$

Here r_1, r_2, r_3 and α_{12}, α_{13}, α_{23} indicate changes in the B—F distances and F—B—F angles for those vibrations which take place solely in the plane of the molecule. The distance of the B-atom from the plane of the molecule is represented by z_4, while z_1, z_2, and z_3 stand for the similar F distances.

C_2D_4

The symmetry coordinates were:

A_{1s} ν_{rs}: $R_1=(r_1+r_2+r_3+r_4)/2$,

ν_{2rs}: $R_2=r_5$,

δ_{rs}: $R_3=(2\alpha_1+2\alpha_2-\beta_1-\beta_2-\beta_3-\beta_4)/12^{\frac{1}{2}}$;

B_{1a} ν_{ra}: $R_4=(r_1+r_2-r_3-r_4)/2$,

δ_{ra}: $R_5=(\alpha_1-\alpha_2-\beta_1-\beta_2+\beta_3+\beta_4)/6^{\frac{1}{2}}$;

B_{2s} $\nu_{\sigma s}$: $R_6=(r_1-r_2+r_3-r_4)/2$,

$\delta_{\sigma s}$: $R_7=(\beta_1-\beta_2+\beta_3-\beta_4)/2$;

B_{3a} $\nu_{\sigma a}$: $R_8=(r_1-r_2-r_3+r_4)/2$,

$\delta_{\sigma a}$: $R_9=(\beta_1-\beta_2-\beta_3+\beta_4)/2$.

In these equations the change in the C=C distance is given by r_5, while r_1, r_2, r_3, and r_4 are the changes in the C—H distances. The changes in the H—C—H angles are denoted by α_1 and α_2; β_1, β_2, β_3, and β_4 are the alterations in the H—C=C angles. The angles and distances at one end of the molecules are α_1, β_1, β_2, r_1 and r_2. The other frequencies (δ, $\delta_{\sigma' a}$, $\delta_{\sigma' s}$) are either completely inactive or uncertain at present.

C_2D_6

The symmetry coordinates for the staggered (D_{3d}) form are:

A_{1g}: $R_1=(r_1+r_2+r_3+r_1'+r_2'+r_3')/6^{\frac{1}{2}}$,

$R_2=(\alpha_{12}+\alpha_{23}+\alpha_{13}-\beta_1-\beta_2-\beta_3+\alpha_{12}'+\alpha_{23}'+\alpha_{13}'-\beta_1'-\beta_2'-\beta_3')/12^{\frac{1}{2}}$,

$R_3=r_4$;

A_{2u}: $R_5=(r_1+r_2+r_3-r_1'-r_2'-r_3')/6^{\frac{1}{2}}$,

$R_6=(\alpha_{12}+\alpha_{23}+\alpha_{13}-\beta_1-\beta_2-\beta_3-\alpha_{12}'-\alpha_{23}'-\alpha_{13}'+\beta_1'+\beta_2'+\beta_3')/12^{\frac{1}{2}}$;

E_u: $R_{7a}=(r_1-r_2-r_1'+r_2')/2$,

$R_{7b}=(r_1+r_2-2r_3-r_1'-r_2'+2r_3')/12^{\frac{1}{2}}$,

$R_{8a}=(\alpha_{23}-\alpha_{13}-\alpha_{23}'+\alpha_{13}')/2$,

$R_{8b}=(\alpha_{23}+\alpha_{13}-2\alpha_{12}-\alpha_{23}'-\alpha_{13}'+2\alpha_{12}')/12^{\frac{1}{2}}$,

$R_{9a}=(\beta_1-\beta_2-\beta_1'+\beta_2')/2$,

$R_{9b}=(\beta_1+\beta_2-2\beta_3-\beta_1'-\beta_2'+2\beta_3')/12^{\frac{1}{2}}$;

E_g: $R_{10a}=(r_1-r_2+r_1'-r_2')/2$,

$R_{10b}=(r_1+r_2-2r_3+r_1'+r_2'-2r_3')/12^{\frac{1}{2}}$,

$R_{11a}=(\alpha_{23}-\alpha_{13}+\alpha_{23}'-\alpha_{13}')/2$,

$R_{11b}=(\alpha_{23}+\alpha_{13}-2\alpha_{12}+\alpha_{23}'+\alpha_{13}'-2\alpha_{12}')/12^{\frac{1}{2}}$,

$R_{12a}=(\beta_1-\beta_2+\beta_1'-\beta_2')/2$,

$R_{12b}=(\beta_1+\beta_2-2\beta_3+\beta_1'+\beta_2'-2\beta_3')/12^{\frac{1}{2}}$.

The changes in the C—H distances are denoted by r_1, r_2, r_3, r_1', r_2', and r_3', and the C—C distance by r_4. The changes in the H—C—C angles are β_1, β_2, β_3, β_1', β_2', and β_3', while the H—C—H angles are α_{12}, α_{23}, α_{13}, α_{12}', α_{23}', and α_{13}'. The unprimed quantities are transformed into the primed quantities by inversion through the center of symmetry.

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Thermodynamic Properties of Ethylbenzene Vapor from 300° to 1500°K

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In this paper are presented tables of the more important thermodynamic functions of ethylbenzene in the ideal gas state from 300° to 1500°K. These functions were calculated using spectroscopic, structural, and calorimetric data. Six investigations of the Raman spectrum of ethylbenzene and three of the infra-red absorption spectrum were available for an assignment of frequencies to the intramolecular vibrations. Included in the paper is a calculation from calorimetric data of the enthalpy and entropy of saturated vapor at 294°K relative to the solid at 0°K. This paper completes a report on a determination of the thermodynamic properties of ethylbenzene covering the solid, liquid, and vapor phases, extending from 0° to 1500°K. All the experimental results are presented in detail in preceding papers.

I. INTRODUCTION

THIS paper completes a report on a determination of the thermodynamic properties of ethylbenzene covering the solid, liquid, and vapor phases and extending from 0° to 1500°K. Properties of the solid and liquid phases from 0° to 300°K are reported in an earlier paper,[1] and a calorimetric measurement of the specific heat of the vapor at 373.16°K in still another paper.[2] The present paper covers the vapor, in the ideal gas state, from 300° to 1500°K.

The calorimetric data on the solid and liquid[1] were used to obtain a so-called calorimetric value for the entropy of ethylbenzene at 294°K in the ideal gas state, relative to the solid at 0°K. This entropy value and the calorimetric value for the specific heat of the vapor[2] were used with spectroscopic and structural data for ethylbenzene to calculate the tables of thermodynamic data for gaseous ethylbenzene presented here. The frequencies of the intramolecular vibrations of ethylbenzene used in these calculations were taken insofar as possible from the infra-red absorption and Raman spectra of ethylbenzene. Other frequencies were derived or were assumed to be the same as for the corresponding motions in closely related compounds. The frequency assignment for toluene by Pitzer and Scott[3] facilitated the interpretation of the ethylbenzene spectra. The barriers restricting internal rotation of the methyl and ethyl groups in ethyl benzene, used in the thermodynamic calculations, were selected to obtain the best agreement between the spectroscopic and calorimetric values for the entropy and specific heat of the vapor. The barriers thus obtained were 2700 and 1300 cal. mole^{-1} for the methyl and ethyl groups, respectively.

Included in the paper is a calculation from calorimetric data of the enthalpy and entropy of saturated ethylbenzene vapor at 294°K relative to the crystalline solid at 0°K.

II. CALORIMETRIC VALUES OF THE ENTHALPY AND ENTROPY OF THE VAPOR

Table I is a summary of the calculations of the enthalpy and entropy of ethylbenzene vapor, relative to the solid at 0°K.

The enthalpy and entropy of saturated vapor were calculated for the temperature, 294°K, at which the heat of vaporization had been measured calorimetrically. The calorimetric data for these calculations were taken from the earlier paper.[1]

The differences between the properties of the real and ideal gases were computed using the Berthelot equation of state and thermodynamic relations for $(\partial S/\partial p)_T$ and $(\partial H/\partial p)_T$. The for-

[1] Russell B. Scott and Ferdinand G. Brickwedde, "Thermodynamic Properties of Solid and Liquid Ethylbenzene, 0° to 300°K," J. Research Nat. Bur. Stand. **35**, Dec. (1945).

[2] Russell B. Scott and Jane W. Mellors, "Specific Heats of Gaseous 1,3-Butadiene, Isobutene, Styrene and Ethylbenzene," J. Research Nat. Bur. Stand. **34**, 243 (1945).

[3] Kenneth S. Pitzer and Donald W. Scott, "The Thermodynamics and Molecular Structure of Benzene and Its Methyl Derivatives," J. Am. Chem. Soc. **65**, 803 (1943).

mulas for the differences are:

$$H^0-H_{\text{sat. vap}}=\int_{p_{\text{sat.}}}^{0}\left(\frac{\partial H}{\partial p}\right)_T dp$$

$$=-\frac{9}{128}RT_c\left(1-18\frac{T_c^2}{T^2}\right)\frac{p_{\text{sat.}}}{p_c} \quad (1)$$

and

$$S^0_{(1\text{ atmos.})}-S_{\text{sat. vap}}$$

$$=\int_{p_{\text{sat.}}}^{p^*}\left(\frac{\partial S}{\partial p}\right)_T dp+R\ln_e\frac{p^*}{p_{(1\text{ atmos.})}}$$

$$=R\left[\ln_e\frac{p_{\text{sat.}}}{p_{(1\text{ atmos.})}}+\frac{27}{32}\frac{T_c^3}{T^3}\frac{p_{\text{sat.}}}{p_c}\right], \quad (2)$$

where the superscript ^{0} refers to the ideal gas state and p^* is a pressure so low that ethylbenzene vapor is essentially an ideal gas. The critical constants used in the Berthelot equation were $T_c=619.6$°K and $p_c=38.1$ atmospheres, as reported by Altschul.[4]

TABLE I. Summary of calculations of enthalpy and absolute entropy of ethylbenzene vapor. [The superscript (0) designates the ideal gas state. E_0^0 is the internal energy of solid ethylbenzene at 0°K. 1 cal. = 4.18330 int j. Atomic weights: C = 12.010, H = 1.0080.]

Enthalpy	cal. mole^{-1}
$H_{\text{sat. liq}}-E_0^0$ at 294°K	9,434.
L_v at 294°K	10,155.
$H_{\text{sat. vap}}-E_0^0$ at 294°K	19,589.
$H^0-H_{\text{sat. vap}}$ at 294°K	1.5
$H^0-E_0^0$ at 294°K	19,590.
$H^0_{298.16\text{°K}}-H^0_{294\text{°K}}$	127.1
$H^0_{298.16\text{°K}}-E_0^0$	19,717.
Entropy	**cal. mole^{-1} °K^{-1}**
$S_{\text{sat. liq}}$ at 294°K	60.40
$\Delta S_{\text{vaporization}}(=L_v/294)$	34.54
$S_{\text{sat. vap}}$ at 294°K	94.94
$S^0_{1\text{ atmos.}}-S_{\text{sat. vap}}$ at 294°K	−9.17
$S^0_{1\text{ atmos.}}$, 294°K	85.77
$S^0_{1\text{ atmos., }298.16\text{°K}}-S^0_{1\text{ atmos., }294\text{°K}}$	0.429
$S^0_{1\text{ atmos., }298.16\text{°K}}$	86.20

[4] Michael Altschul, "On the Critical Constants of Some Organic Compounds," Zeits. f. physik. Chemie **11**, 576 (1893).

Tables V and VI were used to compute the increases in enthalpy and entropy from 294°K to the standard reference temperature 298.16°K (25°C).

III. THE MEASURED SPECIFIC HEAT OF THE VAPOR AT 373.16°K

The specific heat C_p of ethylbenzene vapor measured at 373.16°K with a flow calorimeter has already been reported in detail.[2] The calorimeter was of the adiabatic type in which measurements were made in a steady state of the change in temperature of a stream of ethylbenzene vapor after passage over an electric heater in which electrical energy was dissipated at a constant measured rate.

The experimental values for C_p at 373.16°K are 38.22±0.20 cal. mole^{-1} deg.$^{-1}$ at the pressure of the measurement, 175 mm Hg, and 38.06 ±0.20 cal. mole^{-1} deg.$^{-1}$ at zero pressure or for the ideal gas state.

IV. THERMODYNAMIC FUNCTIONS, 300° TO 1500°K, FROM SPECTROSCOPIC DATA

1. Intramolecular Vibrational Frequencies

There have been six independent investigations of the Raman spectrum of ethylbenzene and three of its infra-red absorption spectrum. All intramolecular vibrations are active in both the Raman and the infra-red absorption spectra. The observed spectral frequencies to 1700 cm^{-1} are listed in Tables II and III. Numbers and letters in parentheses after frequency values are the measures of intensity reported by the original investigators. No Raman polarization data are available. Apparently no complete assignment of frequencies to the intramolecular vibrations of ethylbenzene exists in the literature. The assignment adopted for the thermodynamic calculations is given in Table IV, where the frequencies of toluene and benzene are given for comparison. Ethylbenzene frequencies in parentheses were not observed. These were derived or were assumed to be the same as for the corresponding motions in closely related compounds. Except for the C—H stretching vibrations, the frequencies were taken insofar as possible from the ethylbenzene spectra.

The frequency 290 cm^{-1} for the phenyl vibration 18B of ethylbenzene was obtained from a

TABLE II. Reported Raman frequencies in cm^{-1} of liquid ethylbenzene from 0 to 1700 cm^{-1}.

Dadieu and Kohlrausch[a] (1929)	Ganesan and Venkateswaren[b] (1929)	Söderqvist[c] (1929)	Signer and Weiler[d] (1932)	Reitz and Stockmair[e] (1935)	Dupont and Dulou[f] (1936)
153(4*br*)	153(4)	154(0)		152(6)	149, 166 (*b*6)
	305(0)				
	399(0)				
	447(0)		457(0)		
482(2)			490(1)	483(2)	488(*f*3)
	539(0)		538(0)		
555(1/2)				547(1/2)	555(*f*1)
620(2)	619(0)	620(1)	620(2)	619(3)	622(8)
			724(0)		
					748(2)
766(4)	770(2)	769(2)	773(0)	766(5)	769(12)
				833(1/2)	843(*f*1)
				900(1/2)	904(*f*1)
					948(2)
960(2)	972(0)	964(0)	962(0)	965(3)	968(*f*3)
1001(8)	1005(2)	1002(4)	1000(4)	1002(8)	1004(20)
1028(3)	1031(0)	1030(2)	1032(2)	1029(4)	1032(12)
		1064(0)	1057(0)	1063(1/2)	1067(*f*3)
			1106(0)		
1156(3*br*)	1153(0)	1157(0)	1156(1)	1154(1)	1157(3)
			1176(1)		1179(*f*2)
1192(2*br*)	1203(2)	1203(2)	1204(3)	1199(5)	1203(12)
			1260(1)		
					1288(*b*2)
				1320(0)	1328(*b*2)
1386(0*br*)			1381(0)		1390(*b*1)
1444(3*br*)	1456(0)		1448(1*dd*)	1446(3)	1439, 1460 (*b*4)
			1465(1*dd*)		
			1587(1)	1587(0)	1585(3)
1603(5)	1609(0)	1605(2)	1608(3)	1604(5)	1608(12)

[a] Dadieu and Kohlrausch, Monatsh. **53–54**, 282 (1929).
[b] Ganesan and Venkateswaren, Indian J. Phys. **13**, 195 (1929).
[c] Söderqvist, Zeits. f. Physik **59**, 446 (1929).
[d] Signer and Weiler, Helv. Chim. Acta **15**, 649 (1932).
[e] Reitz and Stockmair, Monatsh. **67**, 92 (1935).
[f] Dupont and Dulou, Bull. soc. chim. **3**, 1639 (1936).

graph, Fig. 1, of the observed frequencies of the 18*B* vibration of a benzyl series of compounds $C_6H_5 \cdot CH_2 \cdot X$ with X=H, SH, Cl, Br, and I, respectively. The vibration 16*A* which appears only weakly in the Raman spectra of benzene and toluene was not observed in the ethylbenzene spectrum. However, the motion of the 16*A* vibration of the phenyl group does not appreciably involve the attached group, as may be seen from Fig. 2, and, hence, the toluene and ethylbenzene frequencies are undoubtedly very nearly the same. The frequencies 486 cm^{-1} and 550 cm^{-1} were assigned to 6*A* and 16*B*, respectively, on the basis of the regular variation of the frequencies of the 6*A* and 16*B* vibrations found for a series of other benzyl compounds.[5] Differences in frequency between corresponding phenyl vibrations of toluene and ethylbenzene are small for vibrations greater than 600 cm^{-1}.

The ethyl group frequencies could not be as completely determined from the ethylbenzene spectrum as could the phenyl frequencies. The internal C—C stretching frequency is prominent in both the Raman and infra-red absorption spectra. A frequency of 365 cm^{-1} was assigned to the $C_{ph}-C-C$ angle bending motion on the basis of other compounds. There are lines 1385, 1450 and 1500 cm^{-1} in the ethylbenzene spectrum corresponding closely to lines in the toluene spectrum assigned by Pitzer and Scott[3] to the CH_3 group in toluene. The corresponding assignment was made for ethylbenzene. The frequencies of the other intra-group vibrations of C_2H_5 taken from the ethylbenzene spectrum approximate the frequencies of those motions in other compounds. Two of the CH_2 frequencies coincide with phenyl group frequencies. The

[5] K. W. F. Kohlrausch, *Ramanspektren* (Akademische Verlagsgesellschaft, Leipzig, 1943). Lithoprinted by J. W. Edwards. Section 46.

TABLE III. Frequencies in cm^{-1} of centers of infra-red absorption bands in ethylbenzene vapor, 480–1700 cm^{-1}.

Lambert and Lecomte[a] (1932)	Stair and Coblentz[b] (1935)	Lambert and Lecomte[c] (1938)
		480(*f*)
		567(*F*)
		617(*f*)
682		
704		
	725	
745	742	
780	770	
847	836	
901	903	
969	968	
	985	
1034	1034	
	1085	
	1172	
	1230	
	1282	
	1380	
	1450	
1488		
	1500	
	1592	

[a] Lambert and Lecomte, Ann. de Physik **18**, 329 (1932).
[b] Stair and Coblentz, J. Research Nat. Bur. Stand. **15**, 295 (1935).
[c] Lambert and Lecomte, Ann. de Physik **10**, 503 (1938).

average of the frequencies 725 and 1230 cm^{-1} assigned to the two rocking vibrations of the CH_3 group is in agreement with averages of rocking vibrations of CH_3 groups in other compounds.[5, 6]

The vibration 7*A* is principally C(phenyl)—C(aliphatic) stretching motion. The high value of its frequency, 1203 cm^{-1}, compared with the normal value of about 970 cm^{-1} for a C—C linkage in aliphatic compounds, is attributable to hyperconjugation[7] of the $C_{ph}-C_{ethyl}$ bond with the phenyl radical. The energy hyperconjugation of this bond, or the difference in the heats of hydrogenation of benzene[8] and ethylbenzene,[9] is about 0.9 kcal. $mole^{-1}$. The frequencies of the corresponding 7*A* vibrations in toluene and styrene are 1210 and 1204 cm^{-1}, respectively.

[6] Gerhard Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945).
[7] Robert S. Mulliken, Carol A. Rieke, and Weldon G. Brown, "Hyperconjugation," J. Am. Chem. Soc. **63**, 41 (1941).
[8] G. B. Kistiakowsky, John R. Ruhoff, Hilton A. Smith, and W. E. Vaughan, "Heats of Organic Reactions. IV. Hydrogenation of Some Dienes and Benzene," J. Am. Chem. Soc. **58**, 146 (1936).
[9] M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, and W. E. Vaughan, "Heats of Organic Reactions. V. Heats of Hydrogenation of Various Hydrocarbons," J. Am. Chem. Soc. **59**, 831 (1937).

2. Molecular Structure Data and Moments of Inertia

In ethylbenzene the equilibrium positions of the symmetry planes of the phenyl and ethyl groups are perpendicular to each other. Generally

TABLE IV. Frequencies in cm^{-1} adopted for the normal modes of intramolecular vibration of ethylbenzene, with the frequencies of benzene and toluene for comparison. [Ethylbenzene frequencies in parentheses were not observed. Benzene and toluene frequencies are from a paper by Pitzer and Scott (see reference 3). Phenyl radical vibrations are for convenience identified with benzene vibrations (Fig. 2), though the motions of the atoms for phenyl radical and benzene vibrations differ in amplitude and direction, and in some cases phenyl and benzene vibrations with the same designation may be quite different, as for example the vibrations Nos. 1 and 12 (see p. 823 in reference 2).]

Vibration type		Ethyl-benzene	Toluene	Ben-zene
Phenyl radical or benzene vibration. (For identification of vibrations see Fig. 2.)	11	154	216	671
	18*B*	(290)	340	1037
	16*A*	(405)	405	400
	6*A*	486	521	606
	16*B*	550	467	400
	6*B*	620	622	606
	4	704	695	685
	10*B*	745	730	849
	12	769	785	1011
	10*A*	840	842	849
	17*B*	903	890	985
	5	948	943	1016
	17*A*	985	(985)	985
	1	1003	1002	992
	18*A*	1032	1030	1037
	15	1085	1070	1170
	9*B*	1156	1155	1178
	9*A*	1177	1175	1178
	7*A*	1203	1210	3047
	3	1288	1282	1298
	19*B*	1320	1310	1485
	19*A*	1488	1483	1485
	8*B*	1587	1586	1596
	8*A*	1608	1603	1596
	14	(1630)	1630	1693
	C—H stretching	(3050)		
		(3050)		
		(3050)		
		(3050)		
		(3050)		
$-C_2H_5$, carbon skeleton vibrations	$C_{ph}-CH_2-CH_3$ angle	(364)		
	CH_2-CH_3	968		
$-(CH_2)$-vibrations		1064		
		1156		
		1177		
		1450		
		(2950)		
		(2950)		
$-(CH_3)$-vibrations		725	1060	
		1230	1190	
		1385	1380	
		1450	1455	
		1500	1495	
		(2950)		
		(2950)		
		(2950)		

accepted bond lengths[10] were used for ethylbenzene as follows: C−H, 1.09A; phenyl ring C−C, 1.39A; and ethyl group C−C, 1.54A. The C−C bond joining the aromatic and aliphatic groups was assumed to be 1.45A in keeping with the lengths of C−C bonds shortened by hyperconjugation in other compounds.[11] Generally accepted values were used also for bond angles: 60° and 120° for the phenyl ring and 109°28′ for the ethyl group. Using these molecular constants, the product of the principal moments of inertia of the ethylbenzene molecule is 67.49×10^{-114} g^3 cm^6 and the reduced moments of inertia of the methyl and ethyl groups are 5.24×10^{-40} and 33.5×10^{-40} g cm^2, respectively.

3. Intramolecular Rotation Barriers

Selection of values of 2700 and 1300 cal. mole^{-1} for the barriers restricting internal rotations of the methyl and ethyl groups in ethylbenzene resulted in satisfactory agreement between the calorimetric and spectroscopic values for S^0 and C_p^0 of the vapor. Thus the calculated entropy

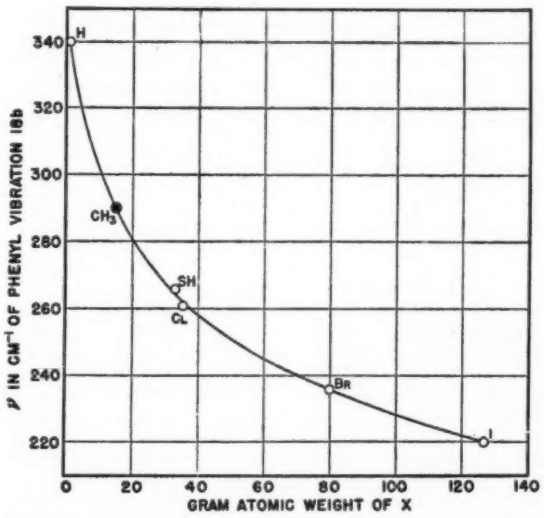

FIG. 1. Dependence on the gram atomic weight of X of the phenyl vibration 18*B* in the series of compounds $C_6H_5CH_2X$. [Data are from Reitz and Stockmair, Monatsh. **67**, 92 (1935) and Bacher and Wagner, Zeits. f. physik Chemie **B43**, 191 (1939).]

[10] Linus Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1942). Chapter V.

[11] Linus Pauling, H. D. Springall and K. J. Palmer, "The Electron Diffraction Investigation of Methylacetylene, Dimethylacetylene, Dimethyldiacetylene, Methyl Cyanide, Diacetylene and Cyanogen," J. Am. Chem. Soc. **61**, 927 (1939).

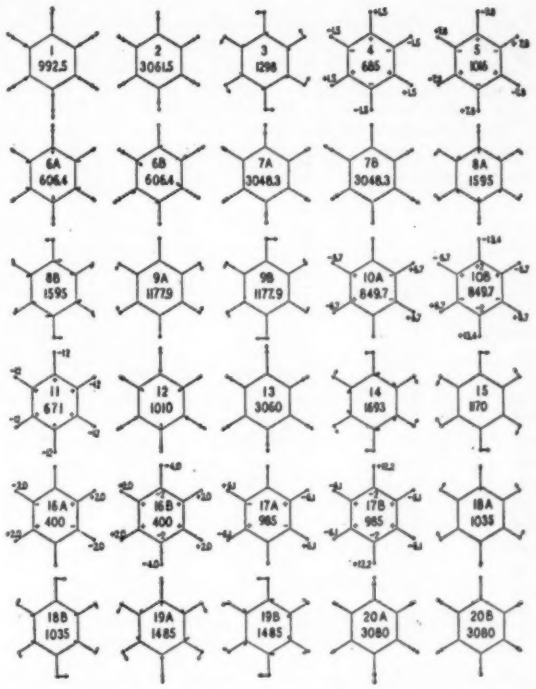

FIG. 2. The frequencies and normal modes of vibration of benzene. + and − refer to motions perpendicular to the plane of the ring. (Reproduced from the paper by Pitzer and D. W. Scott [see reference 3].)

S^0 for the ideal gas state at 294°K and 1 atmosphere pressure is 85.81 cal. mole^{-1} deg.$^{-1}$, while the calorimetric value for the same conditions is 85.77 cal. mole^{-1} deg.$^{-1}$. The calculated specific heat C_p^0 for the ideal gas state at 373.16°K (100°C) is 38.19 cal. mole^{-1} deg.$^{-1}$, whereas the calorimetric value is 38.06 cal. mole^{-1} deg.$^{-1}$. A low value (1300 cal. mole^{-1}) for the barrier restricting rotation of the ethyl group seems reasonable notwithstanding the partial double bond character of the C(aromatic)−C(aliphatic) bond, since a difference in restricting potential around this bond reaches the maximum value for a rotational displacement of only 30° whereas for a normal C(aliphatic)−C(aliphatic) bond the maximum value is reached only for a rotation of 60°. Pitzer and Scott[3] obtained barriers of 500 cal. mole^{-1} restricting rotation of the methyl groups of toluene, and meta- and para-xylene.

4. Tables of Thermodynamic Properties

In Tables V and VI are tabulated the thermodynamic functions for ethylbenzene in the ideal

TABLE V. Thermodynamic functions of ethylbenzene in the ideal gas state. [H^0 and $H_0^0 = E_0^0$ are enthalpies at T°K and 0°K, respectively, referred to the enthalpy of the elements in the standard state at 0°K. ΔH^0 is the enthalpy change of formation from elements in their standard states at T°K. $H_0^0 = E_0^0 = 13{,}580$ cal. mole^{-1}. 25.3770 cal. mole^{-1} = 1 int j g^{-1}. Atomic weights: C = 12.010, H = 1.0080.]

T	$\frac{H^0 - E_0^0}{T}$	H^0	ΔH^0	C_p^0
°K	cal. °C^{-1} mole^{-1}	cal. mole^{-1}	cal. mole^{-1}	cal. °C^{-1} mole^{-1}
298.16	18.037	18960	6830	30.80
300.00	18.116	19020	6790	30.98
400	22.562	22610	4930	40.70
500	27.068	27110	3400	49.20
600	31.367	32400	2180	56.26
700	35.354	38330	1240	62.11
800	39.017	44790	530	67.01
900	42.360	51700	10	71.15
1000	45.421	59000	−340	74.68
1100	48.218	66620	−540	77.70
1200	50.786	74520	−610	80.29
1300	53.145	82670	−570	82.52
1400	55.313	91020	−450	84.45
1500	57.316	99550	−280	86.12

gas state calculated on the basis of the preceding frequency assignment, structural data, and rotation barriers. The contributions to the thermodynamic functions arising from hindered rotation were calculated with the aid of the 1942 tables of Pitzer and Gwinn.[12] Values used for the gas constant R, the radiation constant c_2 (equal to hc/k), and the Avogadro number N_0 were 1.98714 cal. mole^{-1} deg.$^{-1}$, 1.4384 cm deg., and 6.0228×10^{23} mole^{-1}, respectively.

H^0 and F^0 are the enthalpy and free energy of ethylbenzene in the ideal gas state relative to the enthalpy of its elements at 0°K in their standard states, that is the graphitic state for C and the (ideal) gaseous state for H_2. S^0 is the entropy in the ideal gas state, relative to the solid at 0°K. Table values of S^0 and F^0 are for a pressure of one atmosphere.

The internal energy and enthalpy of ethylbenzene in the ideal gas state at 0°K, that is E_0^0 or H_0^0, were calculated using: (1) the value +35,106 cal. mole^{-1} of Prosen and Rossini[13] for $\Delta H^0_{298.16°K}$, the heat of the formation of gaseous styrene from its elements in their standard states at 25°C; (2) the values of Dolliver, Gresham, Kistiakowsky, and Vaughan,[9] −48,931 and −77,498 cal. mole^{-1}, for $\Delta H_{355.16°K}$, the heats of hydrogenation of ethylbenzene and styrene, respectively, to ethylcyclohexane at 355.16°K corrected to the new atomic weight of carbon; (3) 1812 cal. mole^{-1} for the difference between the enthalpies of gaseous styrene at 355.16° and 298.16°K, based on National Bureau of Standards measurements and calculations on styrene; (4) enthalpy differences for ethylbenzene from Table V; and (5) enthalpies of C and H_2 from Woolley *et. al.*[14] The value obtained for E_0^0 of ethylbenzene was 13,580 cal. mole^{-1}.

For the convenience of those desiring values of the enthalpy and free energy of ethylbenzene relative to the enthalpy, E_0^s or H_0^s, of crystalline ethylbenzene at 0°K, Table VII was included. Table VII values of $(H^0 - E_0^s)$ and $(F^0 - E_0^s)$ like Table V and Table VI values of $(H^0 - E_0^0)/T$ and $-(F^0 - E_0^0)/T$ may be combined with other values of E_0^0 based on different heats of

TABLE VI. Thermodynamic functions of ethylbenzene in the ideal gas state at 1-atmosphere pressure. [F^0 and E_0^0 are the free energy at T°K and the internal energy at 0°K, respectively, referred to the internal energy of the elements in their standard states at 0°K. ΔF^0 and K are the free-energy changes and equilibrium constants, respectively, for the reaction forming ethylbenzene from its elements at T°K. $E_0^0 = 13{,}580$ cal. mole^{-1}. 25.3770 cal. mole^{-1} = 1 int j g^{-1}. Atomic weights: C = 12.010, H = 1.0080.]

T	$-\left(\frac{F^0 - E_0^0}{T}\right)$	S^0	$-F^0$	ΔF^0	$\log_{10} K$
					$-\Delta F^0/RT$
°K	cal. °C^{-1} mole^{-1}	cal °C^{-1} mole^{-1}	cal. mole^{-1}	cal. mole^{-1}	2.3026
298.16	68.20	86.24	6760	30910	−22.654
300.00	68.32	86.43	6920	31050	−22.622
400	74.14	96.70	16080	39420	−21.539
500	79.65	106.72	26250	48240	−21.086
600	84.97	116.33	37400	57320	−20.879
700	90.11	125.46	49500	66590	−20.791
800	95.07	134.08	62470	75990	−20.759
900	99.86	142.22	76300	85450	−20.749
1000	104.48	149.90	90900	94960	−20.755
1100	108.95	157.17	106260	104490	−20.761
1200	113.26	164.04	122330	114050	−20.772
1300	117.41	170.56	139060	123600	−20.779
1400	121.43	176.74	156420	133140	−20.785
1500	125.31	182.63	174390	142700	−20.792

[12] Kenneth S. Pitzer and William D. Gwinn, "Energy Levels and Thermodynamic Functions for Molecules with Internal Rotation. I. Rigid Frame with Attached Tops," J. Chem. Phys. **10**, 428 (1942).

[13] Edward J. Prosen and Frederick D. Rossini, "Heats of Formation and Combustion of 1,3-Butadiene and Styrene," J. Research Nat. Bur. Stand. **34**, 59 (1945).

[14] Harold W. Woolley, Morris Moskow, Ferdinand G. Brickwedde, and John G. Aston, "Thermodynamics of Synthetic Rubber and Related Substances. VI. Equilibrium Constants of Some Reactions Involved in the Production of 1,3-Butadiene." A report submitted to the Office of the Rubber Director, War Production Board, March 24, 1944.

reaction to obtain other values of H^0 and F^0 for the investigation of thermodynamic equilibria with other compounds. The Table VII value for $(H^0-E_0^s)$ at 298.16°K was taken from Table I; other Table VII values were obtained by adding 760 cal. mole^{-1} to values of H^0 and F^0 in Tables V and VI.

The heat of vaporization of solid ethylbenzene at 0°K, that is $(E_0^0-E_0^s)$, is 14,340 cal. mole^{-1}.

Stull and Mayfield[15,16] calculated the specific heats C_p^0 of a number of hydrocarbon gases, including ethylbenzene, assuming unrestricted internal rotations around single C–C bonds and summing specific heat contributions for independent vibrations of all the valence bonds of the compound using frequencies whose values are averages for these bonds in a number of compounds. Their values of C_p^0 for ethylbenzene are lower than the C_p^0 values found in Table V, the differences being 1.9 cal. mole^{-1} deg.$^{-1}$ or about 6 percent at 300°K, 1.6 cal. mole^{-1} deg.$^{-1}$ or 3 percent at 500°, 0.50 cal. mole^{-1} deg.$^{-1}$ or 0.6 percent at 1000°K and 0.17 cal. mole^{-1} deg.$^{-1}$ or 0.2 percent at 1500°K. Stull and Mayfield found that for a number of substances the deviations of their values from calorimetric data and more precisely calculated values averaged 4 percent.

TABLE VII. Enthalpy and free energy of ethylbenzene in the ideal gas state relative to the enthalpy, $H_0^s=E_0^s$, of crystalline ethylbenzene at 0°K. [25.3770 cal. mole^{-1} = 1 int j g^{-1}. Atomic weights: C = 12.010, H = 1.0080.]

T	$H^0-E_0^s$	$-(F^0-E_0^s)$
°K	cal. mole^{-1}	cal. mole^{-1}
298.16	19720	6000
300.00	19780	6160
400	23370	15320
500	27870	25490
600	33160	36640
700	39090	48740
800	45550	61710
900	52460	75540
1000	59760	90140
1100	67380	105500
1200	75280	121570
1300	83430	138300
1400	91780	155660
1500	100310	173630

[15] Daniel R. Stull and F. Drew Mayfield, "Heat Capacities of Hydrocarbon Gases," Ind. and Eng. Chem. **35**, 639 (1943).

[16] For principles and methods of calculations see John G. Aston, "The Third Law of Thermodynamics and Statistical Mechanics," Chapter IV in *Treatise on Physical Chemistry*, by H. S. Taylor and Samuel Glasstone (D. Van Nostrand Company, Inc., New York, 1942). Also reference 6, Chapter V, 1.

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The Reaction of Hydrogen Atoms with Acetone*

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The reaction of hydrogen atoms with acetone vapor has been investigated by means of the Wood-Bonhoeffer technique at room temperature. The sole reaction products under these conditions are methane and carbon monoxide. A deuterium exchange experiment showed that the methane product is almost completely deuterized, while undecomposed acetone is exchanged to the extent of 4.1 atom percent. A reaction series has been devised which satisfactorily explains the experimental facts. The activation energy of 9 kcal. found for the over-all process has been assigned to the proposed initiatory step:

$$H+CH_3COCH_3 \rightarrow H_2+CH_3COCH_2.$$

INTRODUCTION

THE reaction

$$H+CH_3COCH_3 \rightarrow \text{products}$$

has not heretofore been the subject of direct investigation, although Rice[1] has predicted an activation energy of about 8 kcal. for a reaction of the type:

$$H+CH_3COCH_3 \rightarrow H_2+CH_3COCH_2-.$$

In the present work, hydrogen atoms produced by the Wood-Bonhoeffer method[2] have been mixed with acetone vapor, and a direct calculation of the reaction energy of the resulting reaction has been possible. By means of a deuterium exchange investigation, evidence has been provided on which to base a reasonable theory for the reaction mechanism.

EXPERIMENTAL METHOD

The discharge tube apparatus was one previously employed in this laboratory.[3] The primary amperage was adjusted to give a secondary current of about 350 milliamperes with a hydrogen pressure of near 0.4 mm. The hydrogen gas was from commercial cylinder supply, and was purified by passage through copper wool at 300°, ascarite, dehydrite, and a liquid-air trap. It was introduced into the apparatus through a fine capillary at a constant pressure slightly above atmospheric. This admitted the gas at a rate of 58 cc/min. at N.P.T. under the high velocity pumping conditions achieved by means of the 4-stage Leybold diffusion pump-Megavac combination. The reaction contact time was calculated to be approximately 0.5 sec. The surfaces of the discharge tube and the 1000 cc reaction vessel were poisoned toward H-atom recombination by means of phosphoric acid. All runs were made at room temperature.

C.P. grade acetone, supplied by City Chemical Corporation, and assayed as 99.5 percent pure, was used without further purification. It was introduced into the reaction chamber inlet through a sintered glass disk mercury cut-off,[4] its pressure in the storage chamber being maintained at 1.9 cm by surrounding the trap containing the liquid phase with an ice-salt bath (temperature approximately −20°). Under these conditions, acetone vapor entered the reaction vessel at a rate of 7 cc/min. with full opening of the sintered glass disk. Slower rates were obtainable at will by partial closing of the disk. The quantity of acetone introduced during any one run was always readily estimated by vapor volume measurements of the total stored material in a three-liter bulb and manometer assembly before and after the runs. No greased connections or stopcocks were used in the storage system.

* Contribution No. 1308 from the National Research Laboratories, Ottawa, Canada.

[1] F. O. Rice and K. K. Rice, *The Aliphatic Free Radicals* Johns Hopkins Press (Baltimore, 1935).

[2] R. W. Wood, Proc. Roy. Soc. (London) **A97**, 455 (1920), **102**, 1 (1922). K. F. Bonhoeffer, Zeits. f. physik. Chemie **113**, 199 (1924), **116**, 391 (1925).

[3] D. J. LeRoy and E. W. R. Steacie, J. Chem. Phys. **12**, 369 (1944).

[4] E. Warrick and P. Fugassi, Ind. Eng. Chem. Anal. Ed. **15**, 13 (1943).

The atom concentrations were at first measured by means of a single Wrede-Harteck[5] gauge situated at the top of the reaction chamber near the inlet from the discharge tube. Later, an additional gauge was installed at the other end of the reaction vessel, at the outlet tube to the traps and pumps. It was found in blank runs that the atom percentage fell off considerably between the two gauges, as expected, but by averaging the two readings, a fairly good estimate of the average atom concentration in the reaction zone was attainable. Other tests were carried out in which nitrous oxide, a gas which is known to be inert to hydrogen atoms,[6] was introduced into the reaction system at a rate closely paralleling the maximum acetone rate. These tests showed that the atom concentration measurements were affected only negligibly by the presence of the heavy foreign gas, at least up to a ratio of 1 cc of nitrous oxide per 8 cc of hydrogen. Accordingly, measurements were made of the atom percentages with and without acetone present in the reaction chamber, the assumption being made that the difference between the two figures should give a reasonable estimate of the proportion of atoms disappearing by reaction with the ketone. This experiment indicated that with the hydrogen stream 20 percent atomic in the absence of acetone, approximately half the atoms disappear by reaction with the ketone when the latter is introduced at the full rate ($\sim$7 cc/min.).

The possibility of more catalysis of atom recombination by acetone adsorbed on the reaction chamber walls was ruled out by the following experiment. The atom concentration was measured with the discharge on but no acetone entering the system. With the discharge off, acetone was admitted at the standard rate for a five-minute period. Its flow was then cut off, and the discharge again turned on. Atom percentage measurements now showed no appreciable change from the preliminary ones, indicating no depoisoning effect due to adsorbed acetone. The figure given in the above paragraph for atoms used up in reaction with acetone can therefore be taken as a true estimate for a gas phase process.

During reaction, undecomposed acetone was collected in a liquid-air trap situated between the reaction vessel and the diffusion pump. It was found during the preliminary runs that no product with an appreciable vapor pressure below dry-ice temperature appeared in this trap. After the run, the quantity of acetone so collected was determined by a vapor volume measurement in a large bulb, thus giving a rough material balance check. A silica gel trap, thoroughly degassed at 100° and cooled in liquid air, was located between the diffusion and Megavac pumps. This served to separate the low boiling gaseous products from excess hydrogen, a method of which Steacie and Phillips[7] have previously made effective use for methane collection.

In the present work, the procedure regularly applied following each run was to evacuate the cold silica gel trap with the diffusion pump system for a ten-minute period. Tests made with measured quantities of carbon monoxide showed that the procedure resulted in no loss of the monoxide, though hydrogen is completely desorbed, fully in accordance with the findings of Lebeau and Marmasse.[8] It was therefore reasonable to assume complete retention of methane also, under the same conditions, since the latter gas has a 30° higher boiling point than carbon monoxide. After the hydrogen separation, the carbon monoxide and methane were Töplered off the gel at 70°, measured, and the mixture analyzed by combustion first on copper oxide wire at 300°, then with admixed oxygen on a platinum filament in the usual manner.

The experiment in which deuterium was substituted for hydrogen was identical in all essential details with the hydrogen runs. The deuterium was from a cylinder supplied by the Stuart Oxygen Company. A preliminary run showed that the gas was contaminated with a considerable percentage of air, but it was found possible to remove all but a small fraction of this impurity by passing the gas through a silica gel

[5] E. Wrede, Zeits. f. Physik **54**, 53 (1929); P. Harteck, Zeits. f. physik. Chemie **A139**, 98 (1928).
[6] K. H. Geib, Ergeb. d. exakt. Naturwiss. **15**, 67 (1936).
[7] E. W. R. Steacie and N. W. F. Phillips, J. Chem. Phys. **4**, 461 (1936).
[8] P. Lebeau and P. Marmasse, Comptes rendus **182**, 1086 (1926).

TABLE I. Experimental results.

Item	Runs with hydrogen 5	6	7	8	9	10	Run with deuterium 2A
Total duration of run (min.)	83.3	83.3	83.3	83.3	83.3	83.3	30
Average percent of atoms (by vol.)	17	20	16	17	14	13	35
Rate of flow of atoms (cc/min. N.P.T.)	10.8	12.9	10.1	10.8	8.7	8.1	24.6
Total vol. acetone passed (cc N.P.T.)	580	600	400	190	335	575	215
Rate of acetone flow (cc/min. N.P.T.)	7.0	7.2	4.8	2.3	4.0	6.9	7.2
Product of flow rates (atoms and acetone)	76	93	49	25	35	56	177
Total vol. gaseous product (cc N.P.T.)	92.2	103.9	66.8	36.6	48.6	74.7	87.6
Percent CO in gaseous product	33.5	33.6	32.7	32.3	33.5	33.3	27.9
Percent methane in gaseous product	66.5	66.4	67.3	67.7	66.5	66.7	55.0
Percent N_2 in gaseous product (D_2 run only)	—	—	—	—	—	—	17.1
Calc. total vol. acetone decomp. (cc N.P.T.)	30.7	34.5	22.3	12.2	16.2	24.9	24.4
Rate of acetone decomp. (cc/min. N.P.T.)	.37	.41	.27	.15	.19	.30	.81
Percent total acetone decomposed	5.30	5.75	5.60	6.45	4.85	4.35	11.35
Average reaction chamber press (mm)	.376	.374	.377	.391	.393	.393	.411
Average room temp. (°C)	24.8	25.0	23.5	22.5	24.0	23.6	24.0
$Z_{H,\ acetone}$ per sec. ($\times 10^{-6}$)	3.1	3.7	2.9	3.3	2.7	2.5	5.0
Collision yield ($\times 10^{8}$)	3.4	3.1	3.9	3.9	3.6	3.5	4.5
Activation energy (kcal.)	8.8	8.8	8.7	8.7	8.8	8.8	8.6
(Rounded average value $-E=9$ kcal.)							

trap at liquid-air temperature prior to entry into the usual hydrogen purification train. Oxygen which escaped this trap was of course removed by combustion on the hot copper wool. The nitrogen passed through the apparatus and appeared in the gaseous reaction products. Its volume was found to be less than 0.5 percent of the total deuterium passed during the run, so it could be assumed to have a negligible effect on the discharge tube phenomena.

RESULTS

The experimental findings for both the H and D atom reactions are summarized in Table I. Collision yields and activation energies have been calculated according to the usual formulae[9] assuming a steric factor of 0.1. Molecular diameters taken were 2.1A for H and D and 6.5A for acetone. The former figure is in accordance with an estimate given Bonhoeffer and Harteck[9] while the latter was calculated from viscosity data.

It is noted that an unusually high atom percentage was obtained in the deuterium experiment as compared to those with hydrogen. This effect is at least partially explainable on the basis of the lower collision rate of the heavier atoms, thus a slower rate of recombination. Otherwise, there is no great difference in the behavior of the two gases in the experiments. That the rates of hydrogen and deuterium flow into the apparatus were approximately equal was evidenced by the reasonably close correspondence of reaction chamber pressure in both types of run.

A rough material balance calculation indicated that the undecomposed acetone must have been free of any appreciable quantity of dissolved heavy product, the relation:

$$\text{Total Vol. Acetone Passed} = \text{Vol. Unreacted Acetone} + 1/3(\text{Vol. CO} + CH_4)$$

being satisfied within 5 percent in all cases. However, not much weight could be attached to these figures because of the large errors involved in the acetone volume measurements relative to the volume of gaseous product. Micro-fractional distillations of some of the residual acetone samples were therefore carried out, and it was found in each case that only a negligible portion of the liquid failed to boil over at 56°, the b.p. of acetone. The trace of residue remaining was only faintly yellow, so could not have contained more than a minute quantity of diacetyl, if any. Most likely it consisted of a small quantity of stopcock grease unavoidably picked up in the transfer of the unreacted acetone to the measuring system.

[9] K. F. Bonhoeffer and P. Harteck, *Photochemie* (Leipzig, 1933).

Tests for diacetyl[10] and for acetonyl acetone[11] were made on samples of unreacted acetone collected from a number of experiments. These gave negative results, and it appears safe to conclude that neither substance is formed in appreciable amount.

The methane and undecomposed acetone from the deuterium run were burned and the samples of water so obtained were analyzed for deuterium content by means of the mass spectrograph. The results of the analyses were as follows:

Methane—99.7 atom percent deuterized (one determination).

Acetone—4.1 atom percent deuterized (two determinations).

DISCUSSION

In Fig. 1, the rate of acetone decomposition for each run is shown plotted against the product of the rates of flow of acetone and of hydrogen or deuterium atoms into the reaction chamber. The very satisfactory linearity of the relationship indicates that the rate-determining step is a simple bimolecular collision process involving the atoms and acetone molecules. The sole detectable products of decomposition under our conditions were methane and carbon monoxide. When atomic deuterium was used, the methane product was almost completely deuterized, while undecomposed acetone was exchanged only to the extent of one atom of deuterium per four molecules of acetone.

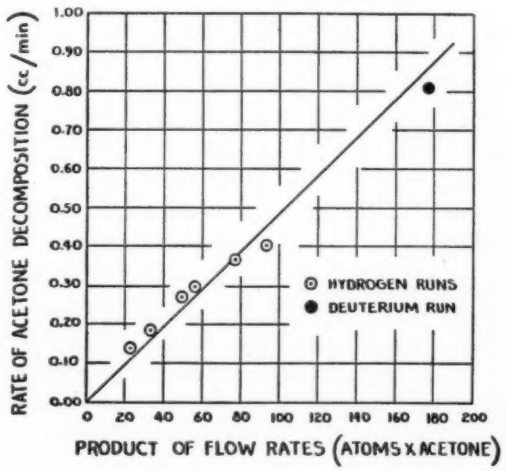

FIG. 1. Relation of reaction rate to concentration of reactants.

The following reaction scheme is proposed to explain the above facts:

$$H+CH_3COCH_3 \rightarrow H_2+CH_3COCH_2, \quad E_{activ}\ 9\ \text{kcal.} \quad (1)$$

$$H+CH_3COCH_2 \rightarrow CH_3COCH_3^*, \quad (2)$$

$$CH_3COCH_3^*+M \rightarrow CH_3COCH_3+M, \quad (3)$$

$$CH_3COCH_3^* \rightarrow CH_3CO+CH_3, \quad (4)$$

$$CH_3CO \rightarrow CH_3+CO \quad \leq 9\ \text{kcal.} \quad (5)$$

$$CH_3 \xrightarrow{H} CH_3\ \text{(exchange)} \quad \text{low} \quad (6)$$

$$CH_3+H \rightarrow CH_4\ \text{(wall or 3rd body)} \quad \text{low} \quad (7)$$

$$CH_3+H_2 \rightarrow CH_4+H \quad \sim 9\ \text{kcal.} \quad (8)$$

In this series, $CH_3COCH_3^*$ represents an activated acetone molecule which has about two chances of losing its excess energy in collision with another (unspecified) molecule to one of undergoing decomposition.

In criticizing the above mechanism, the most obvious question is in regard to the non-appearance of radical recombination products, such as acetonyl acetone, acetyl acetone, diacetyl, and ethane. The answer to this is evident when one considers the fact that the concentrations of the various organic radicals are insignificant as compared to the concentration of hydrogen atoms. Furthermore, Bawn[12] has pointed out that the steric factors for reactions between polyatomic radicals must be considerably less advantageous than for radical-atom combinations. For the above reasons, the rates of the radical-radical reactions will not attain important proportions even on the assumption of very low or zero activation energies.

The activation energy which we have calculated on the basis of the over-all decomposition has been assigned to reaction (1) in accordance with the evidence of Fig. 1. Calculations on the basis of Run No. 2A where both the extent of acetone exchange and of decomposition are known indicate that about $\frac{2}{3}$ of the activated molecules formed in reactions (1) and (2) do not go through the complete decomposition series.

[10] C. R. Barnicoat, Analyst **60**, 653 (1935).
[11] L. Knorr, Ber. **19**, 46 (1886).
[12] C. E. H. Bawn, Trans. Faraday Soc. **31**, 1536 (1935).

However, allowance for this factor alters the magnitude of E but slightly. The effect is therefore neglected, inasmuch as the choice of steric factor is rather arbitrary at the outset.

The value given for E_5 is somewhat open to question. Blacet and Loeffler[13] have reported a figure of 9.6 kcal. for the activation energy of the reaction

$$CH_3CO+M\rightarrow CH_3+CO+M \qquad (9)$$

in reasonable agreement with our assumed maximum. Other estimates have set E_5 between 10 and 20 kcal.[14] It is possible that our reaction (5) should be regarded as occurring as a result of residual energy retained by the acetyl after step (4); a similar postulation to that made by Herr and Noyes[14] in their treatment of the photochemical acetone decomposition. Another alternative is reaction with additional H atoms by a process analogous to reactions (1) and (2), *viz.*

$$H+CH_3CO\rightarrow CH_2CO+H_2, \qquad (10)$$

$$H+CH_2CO\rightarrow CH_3CO^*, \qquad (11)$$

$$CH_3CO^*\rightarrow CH_3+CO. \qquad (12)$$

A third possible explanation of the rapid decomposition of the acetyl radical under our conditions is the reaction

$$H+CH_3CO\rightarrow CH_4+CO. \qquad (13)$$

However, the almost complete deuterization of the methane product of Run No. 2A is then difficult to explain unless it is further assumed that the acetyl radical itself undergoes complete deuterization by the rapid repetition of reactions (10) and (11) or some other fast exchange process prior to the occurrence of reaction (13). This follows from the fact that a number of workers[15] have shown methane to have a high activation energy of exchange with deuterium atoms, though methyl radical deuterization occurs readily at room temperature.[16] Whatever the mechanism of the acetyl split, the non-reaction of the carbon monoxide product with H-atoms is, of course, completely in line with the findings of previous workers.[17]

Which of reactions (7) and (8) is chiefly operative can be decided in the following manner. In the light of available evidence,[18] it appears reasonable to restrict reaction (7) to occurrence only as a wall or third-body process. A rough kinetic calculation indicates that, under our experimental conditions, each CH_3 will on the average make of the order of 10^4 collisions with hydrogen molecules during the time required for it to diffuse to the wall. The presently accepted value for the activation energy of reaction (8) is 9 kcal.,[18] and it can be readily shown that the probability of methane formation by this process is very small as compared to reaction (7), since E_7 is undoubtedly quite low.

The exact mechanism of the exchange process (6) is difficult to envisage on the basis of past evidence. Trenner, Morikawa, and Taylor[15] have proposed both the following schemes as possibilities:

$$CH_3+D\rightarrow CH_3D^*, \qquad (A)$$
$$CH_3D^*\rightarrow CH_2D+H, \text{ etc.};$$

and

$$CH_3+D\rightarrow CH_2+HD, \qquad (B)$$
$$CH_2+D\rightarrow CH_2D, \text{ etc.}$$

An approximate calculation can be made from our experimental results to determine the actual quantity of atoms consumed in reaction with a given amount of acetone. This information can then be applied to the problem of choosing between mechanisms (A) and (B) above.

It was mentioned in connection with the Wrede gauge tests discussed earlier that when acetone entered the apparatus at the full rate (7 cc/min.) and the hydrogen stream was initially 20 percent atoms, about half the latter were used in reaction with acetone. Assuming a similar situation in the case of the deuterium

[13] F. E. Blacet and D. E. Loeffler, J. Am. Chem. Soc. **64**, 893 (1942).

[14] F. O. Rice and K. F. Herzfeld, J. Am. Chem. Soc. **56**, 284 (1934); C. E. H. Bawn, Trans. Faraday Soc. **34**, 598 (1938); E. Gorin, J. Chem. Phys. **7**, 256 (1939); D. S. Herr and W. A Noyes, J. Am. Chem. Soc. **62**, 2052 (1940); H. W. Anderson and G. K. Rollefson, J. Am. Chem. Soc. **63**, 816 (1941); M. H. Feldman, J. E. Ricci, and M. Burton, J. Chem. Phys. **10**, 618 (1942); K. Benson and G. S. Forbes, J. Am. Chem. Soc. **65**, 1399 (1943).

[15] K. H. Geib and E. W. R. Steacie, Zeits. f. physik. Chemie **B29**, 215 (1935); E. W. R. Steacie, Can. J. Research **B15**, 264 (1937); N. R. Trenner, K. Morikawa, and H. S. Taylor, J. Chem. Phys. **5**, 203 (1937).

[16] K. Morikawa, W. S. Benedict, and H. S. Taylor, J. Chem. Phys. **5**, 212 (1937); E. W. R. Steacie, W. A. Alexander, and N. W. F. Phillips, Can. J. Research **B16**, 314 (1938); E. W. R. Steacie and N. A. D. Parlee, Can. J. Research **B17**, 371 (1939).

[17] K. H. Geib and P. Harteck, Ber. **66**, 1815 (1933).

[18] E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York), in press.

experiments, one would also expect half the atoms to take part in the process; that is, a total of 12.3 cc/min. of D atoms for an acetone decomposition of 0.8 cc/min. This assumption seems entirely justified when comparison is made of the results of Runs Nos. 6 and 2A. It is seen that the rates of acetone decomposition almost exactly parallel the relative atom concentrations, the acetone concentrations being the same in the two cases.

Undecomposed acetone passes at the rate of 6.4 cc/min. and is 4.1 atom percent exchanged, i.e., 25 percent of these molecules must undergo reactions (1), (2), and (3). This process eliminates $(6.4/4)\times 2=3.2$ cc/min. of D atoms. Each molecule of acetone which decomposes to methane and carbon monoxide requires 4 D atoms to fulfil steps (1), (2), and (7) of our reaction scheme for a total of $0.8\times 4=3.2$ cc/min. of D atoms. If reactions (10) and (11) are also assumed to be operative, an additional 1.6 cc/min. of D atoms are consumed, making a grand total of 8.0 cc/min. Thus, exclusive of the exchange process (6), only about two-thirds of the total D atoms disappearing can be accounted for at the most.

It therefore can be reasonably concluded that scheme (B) above, or some similar series, must play the major role in methyl radical deuterization, since scheme (A) of itself would promote no change in the apparent atom concentration. This view is supported by the calculations of Gorin, Kauzmann, Walter, and Eyring,[19] who have objected to mechanism (A) on the grounds that the symmetry characteristics of the methane molecule would prevent the concentration of energy in a single C—H bond. Under our conditions, the exchange of the methyls goes nearly to completion since the amount of hydrogen set free in the process is such an extremely small fraction of the total deuterium present.

According to the above conception of the exchange, the methyl radicals act effectively as catalysts for atom recombination. It might be argued that a more complete disappearance of the atoms is therefore to be expected, as was found by Geib and Steacie[15] for the exchange of deuterium with acetylene, where an analogous mechanism was postulated. In the present case, however, atom recombination is not complete owing to two factors: the low relative concentration of methyl radicals, and the rapid removal of the latter by combination with atoms at the wall to give methane, which latter is inert to the atoms.

ACKNOWLEDGMENT

We wish to express our appreciation to Professor H. G. Thode of McMaster University, who kindly carried out the mass spectrographic determinations of deuterium content.

[19] E. Gorin, W. Kauzmann, J. Walter, and H. Eyring, J. Chem. Phys. **7**, 633 (1939).

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The Reaction of Hydrogen Atoms with Dimethyl Mercury*

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The Wood-Bonhoeffer method has been applied to a study of the reaction of hydrogen atoms with dimethyl mercury. The organometallic undergoes rapid decomposition at room temperature, giving as products methane, ethane, and metallic mercury. The variation of the ratio of methane to ethane formation with change in the relative concentrations of reactants has been satisfactorily explained on the basis of a postulated reaction mechanism, all steps in which are assumed to have an activation energy $\leq$6 kcal.

INTRODUCTION

THE reaction of hydrogen atoms with dimethyl mercury has been reported by Cunningham and Taylor[1] in connection with their study of the photo reactions of the organometallic compound. The presence of hydrogen

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[1] J. P. Cunningham and H. S. Taylor, J. Chem. Phys. **6**, 359 (1938).

TABLE I. Experimental results.

Run no.	1	2	3	5
Total duration of run (min.)	20	40	15	60
Proportional opening of valve disk	Full	$\sim\frac{1}{2}$	Full	$\sim\frac{1}{4}$
Vapor pressure of reactant in storage (cm Hg)	1.7	1.7	3.9	1.7
Predicted flow rate of $Hg(CH_3)_2$ (cc/min. N.P.T.)	3.5	1.2	—	0.9
Volume of methane produced (cc at N.P.T.)	43.6	47.1	37.2	61.4
Volume of ethane produced (cc at N.P.T.)	37.7	22.8	48.8	21.0
Calculated vol. $Hg(CH_3)_2$ decomposed (cc at N.P.T.)	59.5	46.4	67.4	51.7
Volume of $Hg(CH_3)_2$ undecomposed (cc at N.P.T.)	8.1	3.1	122	1.1
Calculated total vol. $Hg(CH_3)_2$ passed (cc at N.P.T.)	67.6	49.5	189	52.8
Calculated flow rate of $Hg(CH_3)_2$ (cc/min. N.P.T.)	3.38	1.24	12.6	0.88
Rate of $Hg(CH_3)_2$ decomposition (cc/min. N.P.T.)	2.98	1.16	4.50	0.86
Percentage of $Hg(CH_3)_2$ decomposition	88	92	36	98
Average percentage of H atoms (by vol.)	9	8	10	12
Rate of inflow of atoms (cc/min. N.P.T.)	5.5	4.8	6.1	7.3
Relative value $[H]/[Hg(CH_3)_2]$	1.6	3.9	0.5	8.5
Relative value $\{[H]/[Hg(CH_3)_2]\}^{\frac{1}{2}}$	1.3	2.0	0.7	2.9
Ratio CH_4 formed/C_2H_6 formed	1.2	2.1	0.8	2.9

was found to increase the quantum yield of decomposition. This they explained by postulating the following chain as part of their reaction scheme:

$$CH_3+H_2\rightarrow CH_4+H,$$

and

$$H+Hg(CH_3)_2\rightarrow CH_4+Hg+CH_3.$$

Their experimentally determined activation energy for methane formation was 8.1 kcal. and was assigned to the first of the above reactions, it being inferred that the second step had a somewhat lower value for E. The photochemical decomposition of diethyl mercury[2] was found to proceed in an analogous manner, and similar postulations were made in explanation.

In the present paper, the results are reported of a direct investigation of the second of the reactions given above by the Wood-Bonhoeffer method, and an estimation of the upper limit of its activation energy has been possible. By varying the relative concentrations of atoms and dimethyl mercury, important information concerning the subsequent reactions of the free methyl radicals has been provided.

EXPERIMENTAL METHOD AND RESULTS

The same apparatus as described in a recent report from this laboratory[3] was employed in the present work with little modification. Dimethyl mercury, as prepared by the method of Gilman and Brown,[4] was dried over fused calcium chloride and stored in a trap connected to the reaction chamber inlet through a Warrick-Fugassi valve.[5] As in the previous work,[3] the rate of flow of reactant into the reaction system could be varied at will by adjustment of the disk opening, or by altering the vapor pressure of the stored material. All runs were made at room temperature.

A calibration run showed that with the storage trap immersed in an ice bath at 0°C, the vapor pressure was 1.70 cm under dynamic conditions, and the rate of flow with full opening of the disk was about 3.5 cc/min. at N.P.T. of dimethyl mercury vapor. No provision was made for independently measuring the quantity of reactant introduced during each run, since it was found possible to measure all reaction products accurately, and in no case was the amount of unreacted organometallic large in proportion. It is seen from the results given in Table I above that flow rates of reactant predicted on the basis of the calibration run were satisfactorily realized by the calculated figure in the three comparable cases, indicating a suitable material balance.

Atom concentrations were estimated by means of Wrede-Harteck gauges as previously described.[3] It was always possible to make a suitable estimate of the average atom concentration

[2] W. J. Moore and H. S. Taylor, J. Chem. Phys. **8**, 396 (1940).
[3] G. M. Harris and E. W. R. Steacie, J. Chem. Phys. **13**, 554 (1945).
[4] H. Gilman and R. E. Brown, J. Am. Chem. Soc. **52**, 3314 (1930).
[5] E. Warrick and P. Fugassi, Ind. Eng. Chem. Anal. Ed. **15**, 13 (1943).

in the reaction zone during each run. However, no measurements could be made of the proportion of atoms actually consumed in reaction with dimethyl mercury, because of the rapid contamination of the walls of the reaction chamber with the metallic mercury product. This coating undoutedly catalyzed atom recombination considerably, as was evidenced by the fact that the lower Wrede gauge indicated zero atom concentration throughout and immediately after each run. The de-poisoning layer of mercury was easily removable by running the apparatus for some time with the discharge on and no reactant present. The mercury then distilled out of the reaction chamber into the first liquid-air trap, and the concentration of atoms in the chamber regained its normal magnitude of about 20 percent.

The gaseous reaction products consisted solely of methane and ethane. The undecomposed dimethyl mercury and part of the ethane condensed in the liquid-air trap, while the remaining ethane and the methane were collected in the silica gel trap by the standard method.[3] Ethane and dimethyl mercury were separated by distillation at dry-ice temperature, and methane and ethane by distillation at liquid-air temperature. The quantities of all three products were estimated by vapor volume measurements at room temperature. The composition of the methane and ethane fractions were checked by combustion with oxygen on a platinum filament, the results in each case being in good agreement with theory. Table I summarizes all the pertinent figures obtained in these experiments.

DISCUSSION

The results summarized in Table I show that the reaction of hydrogen atoms with mercury dimethyl is very rapid at room temperature. When sufficient atoms are available, as in Runs 1, 2, and 5, the reaction goes rapidly to near completion. This indicates an activation energy of 6 kcal. or less, assuming the usually accepted steric factor for such processes of 0.1. A second observation of interest is the wide variation of the ratio of methane to ethane formation. This ratio appears to be directly proportional to the square root of the ratio of the relative concentrations of atoms and organometallic compound.

The mechanism proposed to explain the facts is as follows:

$$H+Hg(CH_3)_2\rightarrow CH_4+Hg+CH_3 \qquad E_{act}(\text{kcal.})\leq 6, \quad (1)$$

$$CH_3+Hg(CH_3)_2\rightarrow C_2H_6+Hg+CH_3 \qquad \leq 6, \quad (2)$$

$$CH_3+CH_3\rightarrow C_2H_6 \qquad \text{low}, \quad (3)$$

$$CH_3+H\rightarrow CH_4 \text{ (wall or 3rd body)} \qquad \text{low}. \quad (4)$$

The additional reaction

$$CH_3+H_2\rightarrow CH_4+H \qquad \sim 9 \quad (5)$$

need not be considered under our conditions, as has been pointed out in our previous report.[3]

At the outset, it might be argued, by analogy to the hydrogen atom-acetone reaction,[3] that the initiatory processes in the present study should be of the form:

$$H+CH_3HgCH_3\rightarrow H_2+CH_3HgCH_2, \quad (6)$$

$$H+CH_3HgCH_2\rightarrow CH_3HgCH_3^*, \quad (7)$$

$$CH_3HgCH_3^*\rightarrow CH_3+Hg+CH_3, \quad (8)$$

followed by reactions (3) and (4). However, this latter scheme is disallowed by the data of Run No. 3, an experiment in which the dimethyl mercury molecules considerably outnumbered the available hydrogen atoms. Here, 4.5 cc/min. of $Hg(CH_3)_2$ were decomposed, and methane production was at the rate of 2.5 cc/min. The mechanism of reactions (6), (7), (8), etc. would require at least $(4.5\times 2)+2.5=11.5$ cc/min. of hydrogen atoms, much in excess of our experimental estimate of 6.1 cc/min. of available atoms, which latter figure should itself be taken as a maximum.

The first-mentioned scheme has therefore been accepted as more suitable. The contradiction of the Rice-Teller[6] principle is only apparent, since the structural characteristics of dimethyl mercury cannot reasonably be considered entirely analogous to those of a purely organic molecule such as ethane or acetone. There is every possibility that, in the case of the organometallic, distortion of C—H bonds of the methyl on the approach of an H atom and

[6] F. O. Rice and E. Teller, J. Chem. Phys. 6, 489 (1938).

eventual cleavage of the C—Hg linkage, will occur with fairly low activation energy.

Reaction (2) must be included in the series since otherwise the maximum possible value for the methane/ethane ratio would be 2:1, which is seen to be contrary to the facts. The reaction was postulated by Cunningham and Taylor[1] in order to explain the increasing quantum yield of ethane formation with temperature in their photochemical studies. Their results indicated that the process has a low activation energy, and this conclusion is verified by our work.

Steacie[7] has recently discussed the evidence concerning reaction (3) very fully, and concludes that third body restrictions of some sort may exist, through the evidence is difficult to assess due to the prevalence of surface effects in a good deal of the pertinent research. In the present work, it appears that surface combination of methyls cannot be the major process, since even in Run No. 5, where hydrogen atoms enter the reaction chamber in considerable excess, 40 percent of the mercury dimethyl decomposition is still to ethane. If methyl recombination had to occur at the wall, one would not expect much ethane formation under these conditions, since the probability of occurrence of reaction (4) would considerably overbalance that of reaction (3). It is true, of course, that hydrogen atom recombination is catalyzed by the presence of mercury on the walls, rapidly reducing the effective gas-phase atom concentration to zero as the gas passes through the reaction zone. However, since this catalysis very probably occurs through the agency of adsorption of atoms, it is still difficult to see why methyls which become adsorbed on the wall would react with each other rather than with a hydrogen atom. We therefore favor the homogeneous bimolecular concept for reaction (3).

At this point, it is interesting to make a few quantitative formulations in support of our proposed mechanism. Strictly speaking, a "steady state" calculation is not justified in a flow system such as we have used. However, the rates of inflow of reactants are reasonably constant during any one run, and the time actually spent in the reaction chamber, 0.5 sec., is long as compared to the time required for reactions of low activation energy to go essentially to completion. It therefore does not seem to be stretching the point too much to make some simple kinetic calculations concerning the rates of methane and ethane formation on the basis of our proposed reaction mechanism.

The gas-phase concentration of methyl radicals will, according to our theory, depend mainly on reactions (1) and (3), whence

$$[CH_3]=\{k_1/k_3[H][Hg(CH_3)_2]\}^{\frac{1}{2}}.$$

The ratio of the rates of methane to ethane formation will be given as follows:

$$\frac{d[CH_4]}{dt}\Big/\frac{d[C_2H_6]}{dt}$$

$$=\frac{k_1[H][Hg(CH_3)_2]+k_5[H][CH_3]}{k_2[CH_3][Hg(CH_3)_2]+k_3[CH_3]^2}$$

$$\cong\frac{k_1[H]}{k_2[CH_3]}=\frac{(k_1k_3)^{\frac{1}{2}}}{k_2}\left\{\frac{[H]}{[Hg(CH_3)_2]}\right\}^{\frac{1}{2}}$$

in agreement with our experimental evidence.

[7] E. W. R. Steacie, *Atomic and Free Radical Reactions* (Reinhold Publishing Corporation, New York), in press.

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The Mercury Photosensitized Reactions of Propane at Low Pressures

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The mercury photosensitized reactions of propane have been investigated at room temperature between 0.7 and 84.5 mm Hg. At high pressures the products consisted almost entirely of hexane and hydrogen but at low pressures methane and C_2 and C_4 hydrocarbons were produced in increasing amounts. The production of methane was much less than in the similar reactions of ethane. The effect of pressure on the nature of the reaction can be accounted for by a C—H split followed by atomic cracking and recombination reactions as proposed by Steacie and Dewar, but the difference in the products from propane and ethane make it likely that the reaction proceeds, at least in part, by the formation of an active molecule. At low pressures the rate of propane disappearance is retarded and the extent of C—C split increased by the addition of hydrogen. The effect of added hydrogen is explained by an increase in the rates of recombination of hydrogen atoms and of atomic cracking reactions.

INTRODUCTION

THE reactions of the lower paraffin hydrocarbons photosensitized by $Hg(^3P_1)$ and $Cd(^3P_1)$ atoms have been investigated. Some aspects of these reactions, however, are considered to have received inadequate attention so that further investigation is desirable.

The mercury photosensitized reactions of ethane were investigated in a circulatory system[1,2] and in single pass flow system.[3] In these investigations a trap in the circulatory system was maintained at a low temperature to remove secondary products of the reaction. Steacie and Phillips found that at high trap temperatures the products consisted largely of hydrogen and butane but that with decreasing trap temperatures the production of hydrogen and butane decreased while methane and propane appeared in increasing amounts. They assumed that the initial act was a C—H split:

$$C_2H_6+Hg(^3P_1)\rightarrow C_2H_5+H+Hg(^1S_0)$$

and accounted for the products by the occurrence of the "atomic cracking" reaction:

$$C_2H_5+H\rightarrow 2CH_3$$

followed by radical recombination. The products of the similar reactions of propane,[4] *n*-butane,[5] and iso-butane,[6] investigated under very similar conditions in a circulatory system, consisted almost exclusively of hydrogen and hexanes from propane and of hydrogen, octanes, and dodecanes from the butanes. The nature of the products from iso-butane was found to be independent of the working pressure of the paraffin between 6 and 60 cm whereas with ethane a marked change occurred at pressures of 15 cm and lower.

The products from propane and the butanes as well as from ethane at high pressures are certainly in accord with the assumption of a C—H split as the initial act. Since the C—H bonds in the lower paraffin hydrocarbons are known to be considerably stronger than the C—C bonds, the C—H split found indicates that the reaction is of a specific nature and it has been suggested[7,8] that the reaction probably proceeds by virtue of the formation of HgH. This picture then leads us to believe that, in these reactions, the mercury atom does not play the part of a true sensitizer, i.e., serving only as a medium by which energy is transferred, but actually takes part in the reaction. However, the mechanism proposed to account for the C—C split with ethane at lower pressures does not appear to be adequate since Steacie and Cun-

[1] S. Tolloczko, Przemsyl Chem. **11**, 245 (1927).
[2] E. W. R. Steacie and N. W. F. Phillips, J. Chem. Phys. **6**, 179 (1938); Can. J. Research **B16**, 303 (1938).
[3] E. W. R. Steacie and R. L. Cunningham, J. Chem. Phys. **8**, 800 (1940).
[4] E. W. R. Steacie and D. J. Dewar, J. Chem. Phys. **8**, 571 (1940).
[5] A. W. Hay and C. A. Winkler, Can. J. Research **B21**, 149 (1943).
[6] B. deB. Darwent and C. A. Winkler, J. Phys. Chem. **49**, 150 (1945).
[7] E. W. R. Steacie, Ann. N. Y. Acad. Sci. **41**, 187 (1941).
[8] K. J. Laidler, J. Chem. Phys. **10**, 43 (1942).

ningham[3] found considerable methane in their single pass experiments, in which the H atom concentration was certainly very low. This makes it seem somewhat unlikely that the methane was produced by "atomic cracking." Hence the question arises as to whether the difference in the products from ethane indicates a reaction which differs from the similar reactions of propane and butane in type rather than in degree.

The products of the $Cd(^3P_1)$ sensitized reactions of ethane[9] and propane[10] were found to contain significant amounts of methane. The mechanisms postulated were entirely similar to those that were used to account for the products of the $Hg(^3P_1)$ sensitized reactions but, at least with propane, the products of the reactions with $Hg(^3P_1)$ and $Cd(^3P_1)$ are significantly different. It may be noted that cadmium sensitized reactions occur via CdH, while there is no evidence whether or not HgH is involved in the case of mercury. If methane is produced in both the $Cd(^3P_1)$ and $Hg(^3P_1)$ reactions of propane by atom cracking it is difficult to explain the differences in the products since the reaction:

$$H+C_3H_7\rightarrow C_2H_5+CH_3$$

should be independent of the initial act whereby the H and/or the C_3H_7 is produced. This point is discussed more fully at the end of this paper.

The quantum yields of all of the above reactions are of the order 0.1 to 0.2 which is about 5 to 10 percent of the value that would be expected on the basis of the above mechanism. This inefficiency may be caused by physical effects, such as quenching to the metastable $^3P_0$ state with subsequent degradation and dissipation of the energy as heat, or to recombination reactions of the type

$$H+C_3H_7\rightarrow C_3H_8.$$

However, Steacie, Alexander, and Phillips[11] and Steacie and Parlee,[12] working with deuterium atoms and ethane and propane, respectively, found that the residual ethane and propane were entirely light, which indicates that recombination is not serious. Inefficiency of a physical type is a possibility but its extent is rather surprising.

The present series of investigations were undertaken in an attempt to elucidate some of the above inconsistencies. It seems likely that the difference in the behavior of ethane on one hand and of propane and the butanes on the other to $Hg(^3P_1)$ atoms could be caused only by the relative smallness of the ethane molecule and/or the absence of secondary or tertiary hydrogen atoms in ethane. In any case the above differences should be only in degree since all of the lower paraffin hydrocarbons are essentially similar in behavior. Hence the reaction of $Hg(^3P_1)$ atoms with propane at 30°C was investigated at low pressures with the results reported below.

EXPERIMENTAL

The reaction was investigated in a circulatory system of conventional type in which the heavy products were condensed out in one trap and propane stored as a liquid in another trap at a lower temperature.

The volume of the reaction system, about 740 cc, was made as small as was convenient as semi-micro analytical methods were used to determine whether small amounts of C_2 and C_4 hydrocarbons were produced since these were not detected in the previous investigation of the $Hg(^3P_1)$ reaction of the propane. The reactor was a quartz cell 4.9 cm in diameter and 11.5 cm long provided with plane windows. The lamp was the usual low pressure type filled with 3 mm of neon and a little mercury; it was placed near to the reaction cell from which it was separated by a shutter. The traps were kept at low temperatures, one at −80°C to prevent heavier products from reaching the second which was kept at a temperature low enough to condense propane and provide a constant vapor pressure. The circulating pump was of the type described by Puddington[13] and circulated gas at about 400 cc per min at 760 mm. The saturator was

[9] E. W. R. Steacie and R. Potvin, J. Chem. Phys. **7**, 782 (1939).
[10] E. W. R. Steacie, D. J. Le Roy, and R. Potvin, J. Chem. Phys. **9**, 306 (1941).
[11] E. W. R. Steacie, W. A. Alexander, and N. W. F. Phillips, Can. J. Research **B16**, 314 (1938).
[12] E. W. R. Steacie and N. A. D. Parlee, Can. J. Research **B17**, 371 (1939); Trans. Faraday Soc. **35**, 854 (1939).
[13] I. E. Puddington, Ind. Eng. Chem. Anal. Ed. **17**, 592 (1945).

warmed to about 40°C and the mercury content of the gases was reduced to the equilibrium value at atmospheric temperature by contact with nickel pellets.

The products of the reaction were analyzed by fractionation in an apparatus of the type described by Ward.[14] Tests with synthetic mixtures showed that separations could be accomplished with an accuracy of about ±0.01 cc at 760 mm. Since the production of methane was an important part of this research, special care was taken with the analysis of the hydrogen-methane fraction. The hydrogen was removed by oxidation on copper oxide at 280°–300°C—the residue, methane, was further characterized by combustion with a measured volume of oxygen on a glowing platinum spiral; the volume of oxygen consumed as well as that of carbon dioxide produced were used in determining the composition of the residue. The products containing five or more carbon atoms per molecule were measured as gases at low pressures (up to 30 mm).

The propane used was the product of the Ohio Chemical Company. No methane or other impurities could be detected by our analytical methods so it was subjected only to a simple bulb-to-bulb distillation, the middle ⅓ being retained and stored in a 1-liter flask. Before each run the propane was condensed in liquid air and evacuated to ensure that there was no contamination with air which might have entered through leaks in the stopcocks. A suitable volume of propane was then measured accurately in the gas burette and transferred to the apparatus by condensation in a trap surrounded by liquid air. The lamp was turned on about 30 minutes before each run to ensure constancy of output and the current controlled manually and kept constant at 100 ma.

Some experiments were carried out in the presence of hydrogen. The hydrogen was taken from a cylinder of "electrolytic" hydrogen and purified by passage over heated copper followed by a trap in liquid air.

[14] E. C. Ward, Ind. Eng. Chem. Anal. Ed. **10**, 169 (1938).

RESULTS

The results of this investigation are given in the accompanying tables and illustrated graphically. The conditions under which the experiments were conducted and the amounts of the various products obtained are listed in Table I. The method of analysis used allowed accurate

TABLE I. Experimental conditions and results. Volume of system = 740 cc; current to lamp = 100 ma.

Run no.	Working pressure of C_3H_8 mm Hg	Time of run hr.	Initial reactants C_3H_8 cc	Initial reactants H_2 mm	Products—cc H_2	CH_4	C_2	C_3	C_4	C_5^+
1	5.0	2.0	24.89	—	1.74	0.65	0.16	20.29	0.25	—
2	84.5	1.0	133.3	—	6.96	0.06	0.07	119.8	0.08	6.55
3*	8.5	1.0	10.72	—	1.78	0.15	0.08	7.35	0.08	1.38
4*	7.5	1.5	7.58	—	1.66	0.25	0.10	4.49	0.07	1.19
5*	15	1.0	19.85	—	2.11	0.11	0.10	15.68	0.08	1.90
6	3	3.0	12.27	—	0.56	1.22	0.26	9.06	0.36	1.06
7	3	1.0	6.925	—	0.38	0.39	0.16	5.48	0.23	0.70
8	3	5.0	20.40	—	1.81	1.99	0.73	13.22	0.19	2.66
9	3	3.0	12.60	—	1.35	1.15	0.45	7.87	0.14	2.15
9(*a*)**	3.34	3.0	16.26	—	2.72	0.54	0.17	11.38	0.35	—
10	0.72	3.0	12.73	10.0	8.34	1.07	0.03	12.19	0.04	0.10
12	0.73	3.0	12.21	5.0	6.50	1.21	0.06	11.68	0.06	0.06
13	0.70	3.0	10.40	1.34	1.37	1.91	0.27	9.07	0.23	0.11
14	0.79	3.0	10.69	0.00	0.14	1.26	0.26	8.01	0.59	0.60
15	3.35	2.0	10.15	0.00	0.73	0.80	0.142	7.27	0.372	1.11
16	3.25	2.0	10.41	29.7	—	0.77	0.065	9.59	0.097	—
17	3.38	2.0	8.18	6.83	—	1.11	0.097	7.00	0.217	0.359
18	0.76	3.0	5.63	2.75	1.47	1.79	0.202	4.33	0.143	0.091
19	3.21	2.0	5.885	2.75	—	1.09	0.152	4.34	0.246	0.449
20	0.658	3.0	6.575	0.00	0.143	1.30	0.266	3.987	0.592	—
21	18.	1.0	30.09	—	2.95	0.162	0.091	24.93	0.00	2.56
22	6.5	1.0	10.30	—	1.28	0.34	0.0972	7.344	0.162	1.36

*Runs done without cold trap. The working pressure quoted is the average of the initial and final pressure of propane.
** Volume of apparatus = 4115 cc.

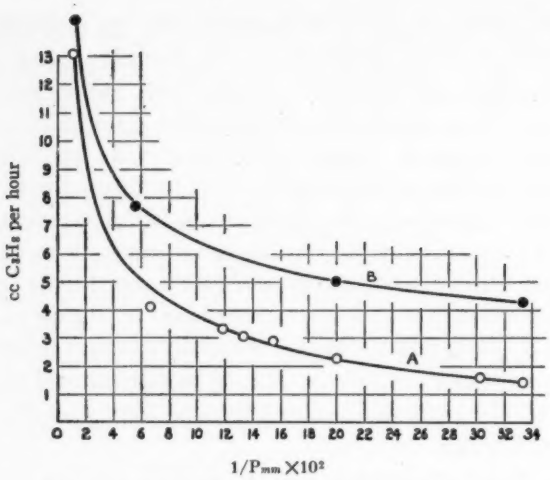

FIG. 1. Effect of working pressure of propane on rate of reaction. A = uncorrected rate and B = rate corrected for incomplete quenching.

measurement of the methane and C_2 fraction since the hydrogen and methane could be separated completely from the C_2 fraction and, by combustion of the residual hydrocarbon, after removal of the hydrogen on copper oxide, we could estimate the amount of C_2 that had been taken over with the methane. Combustion showed that the residual methane was very seldom contaminated by C_2 hydrocarbons and in no case was this contamination serious. Similarly the C_2 fraction could contain only C_3 hydrocarbons as impurities and the extent of contamination was again estimated by combustion. The purity of the C_3, C_4, and C_5 fractions was not estimated by combustion since the large volume of residual propane made the accurate determination of small amounts of C_4 impurity a virtual impossibility by the method used and the C_4 fraction may have been contaminated by C_3 and C_5 hydrocarbons which could not be determined by combustion. Accordingly much more reliance can be placed in the figures quoted for the volumes of hydrogen, methane, and C_2 hydrocarbons than for the rest. In nearly all cases the combustion of the C_2 fraction indicated the likelihood that ethylene was an important constituent; the C_2 fraction from run 6 analyzed to $C_{1.96}H_{3.8}$. The gas volumes reported were corrected to 760 mm and room temperature (25°–27°C).

The effect of the working pressure of propane on the course of the reaction is shown in Table II and illustrated in Figs. 1 and 2. Curve A of Fig. 1 illustrates the effect of pressure on the rate of decomposition of propane; Curve B shows that the rate of disappearance of propane decreases with decreasing pressure even when corrections are applied to allow for decreased quenching. Figure 2 illustrates the linear relationships that exist between the yields of the products and the reciprocal of the working pressure of propane; the yields of hydrogen and C_5^+ hydrocarbons are decreased whereas those of CH_4, C_2, and C_4 hydrocarbons are increased as the propane pressure is decreased.

The effect of including a cold trap to remove the heavy products and to provide a constant working pressure of propane is demonstrated in Figs. 1 and 2 which show that in the absence of a cold trap the yield of hydrogen per cc of propane

TABLE II. Effect of pressure on the reaction. Conditions as in Table I.

Run no.	Working press. of C_3H_8 mm	Reaction rate cc C_3H_8 reacted per hr.	Production—cc/hr.					cc produced/cc C_3H_8 reacted				
			H_2	CH_4	C_2	C_4	C_5^+	H_2	CH_4	C_2	C_4	C_5^+
2	84.5	13.1	6.72	0.06	0.07	0.08	6.32	0.515	0.004	0.005	0.006	0.485
21	18.0	5.16	2.95	0.162	0.091	0.00	2.56	0.571	0.0314	0.0176	0.000	0.495
5*	15.0	4.16	2.11	0.11	0.10	0.08	1.90	0.506	0.026	0.024	0.019	0.455
3*	8.5	3.37	1.78	0.15	0.08	0.08	1.38	0.53	0.045	0.024	0.024	0.41
4*	7.5	3.09	1.11	0.17	0.07	0.05	0.79	0.536	0.081	0.032	0.023	0.384
22	6.5	2.96	1.28	0.34	0.097	0.145	1.36	0.431	0.145	0.0329	0.0545	0.46
1	5.0	2.30	0.87	0.33	0.08	0.12	—	0.377	0.142	0.035	0.055	—
9(a)*	3.3	1.63	0.91	0.18	0.06	0.12	—	0.556	0.11	0.035	0.0715	—
A**	3.0	1.40	0.35	0.40	0.12	0.15	0.56	0.250	0.285	0.086	0.107	0.40
14	0.75	0.89	0.05	0.42	0.09	0.20	0.20	0.056	0.472	0.101	0.225	0.225
20	0.658	0.863	0.048	0.43	0.089	0.197	—	0.055	0.504	0.103	0.231	—

* Runs without cold trap.
** Average of runs 6, 7, 8, 9, 15.

decomposed increases and that of C_5^+ hydrocarbon decreases with decreasing pressure of propane. This effect is the opposite to that found when a cold trap was used. The absence of a cold trap does not change either the rate of reaction (Fig. 1) nor the production of C_2 and C_4 hydrocarbons.

The effect of the duration of the run on the nature of the reaction is shown in Table III and Fig. 3. It is seen that rates of decomposition of propane and of production of hydrogen and methane are independent of the length of the run. The effect of the length of run on the production of C_4 and C_5^+ hydrocarbon is somewhat erratic but may be taken as constant within experimental error.

The effect of the addition of hydrogen is shown in Table IV and in Fig. 4. The effect of hydrogen on the reaction is quite evident from these results and will be discussed later. We find that the addition of hydrogen does affect markedly the nature of the reaction but that, in the runs at 3.2 mm, the accumulation of hydrogen in the system as the run progresses does not alter the nature of the reaction (Fig. 3); this is understandable when we realize that the amount of hydrogen produced is small compared to the amounts added and that the effect would probably not be detectable with the methods used for analyzing and measuring the fractions.

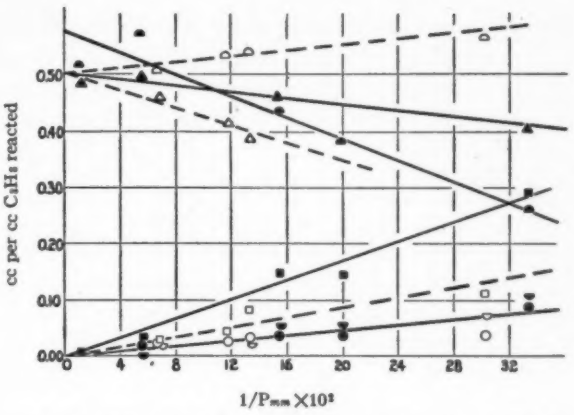

FIG. 2. Effect of working pressure of propane on the reaction. ▲ = hydrogen, ▲ = C_5^+, ■ = CH_4, ● = C_2, ▼ = C_4, and open points = runs without cold trap.

DISCUSSION

The results of this investigation indicate that the following points are of significance in establishing the mechanism of the reactions of the lower paraffin hydrocarbons with active mercury atoms: (*a*) At high propane pressures the products consist almost entirely of hydrogen and

TABLE III. Effect of time of run on the reaction at 3-mm propane pressure. Conditions as in Table I.

Run no.	Time hr.	Rate cc/hr.	Production—cc/hr. H_2	CH_4	C_2	C_4	C_5^+	Production—cc/cc C_3H_8 reacted H_2	CH_4	C_2	C_4	C_5^+
7	1	1.45	0.38	0.39	0.16	0.23	0.70	0.26	0.27	0.11	0.16	0.48
15	2	1.44	0.36_5	0.40	0.07	0.18_6	0.55_5	0.25_4	0.277	0.05	0.13	0.36
6	3	1.07	0.19	0.41	0.09	0.12	0.35	0.17	0.38	0.08	0.11	0.33
9	3	1.58	0.44	0.38	0.15	0.05	0.72	0.27_5	0.24_3	0.09_5	0.03	0.45
8	5	1.36	0.36	0.40	0.15	0.04	0.53	0.27	0.29	0.11	0.03	0.39

TABLE IV. Effect of hydrogen on the reaction. Conditions as in Table I.

Run No.	H_2 added mm	Reaction rate	Production—CC/hr. CH_4	C_2	C_4	C_5^+	cc product/cc C_3H_8 reacted CH_4	C_2	C_4	C_5^+
			(*a*) Working pressure of propane = 3.2 to 3.4 mm							
15	0.00	1.44	0.40	0.071	0.186	0.55	0.277	0.049	0.129	0.358
19	2.75	0.772	0.54_5	0.076	0.123	0.224	0.71	0.097	0.16	0.29
17	6.83	0.59	0.56	0.049	0.109	0.179	0.94	0.082	0.184	0.304
16	29.7	0.41	0.39	0.032	0.049	—	0.94	0.039	0.18	—
			(*b*) Working pressure of propane = 0.70 to 0.80 mm							
14	0.00	0.893	0.42	0.09	0.19	0.20	0.47	0.097	0.22	0.22
13	1.34	0.44	0.64	0.09	0.08	0.04	1.43	0.20	0.17	0.08
18	2.75	0.43	0.59_7	0.06_7	0.04_8	0.03	1.38	0.15_5	0.11	0.07
12	5.0	0.18	0.40	0.02	0.02	0.02	2.28	0.13	0.13	0.13
11	10.0	0.14	0.36	0.01	0.01	0.03	2.55	0.071	0.095	0.237

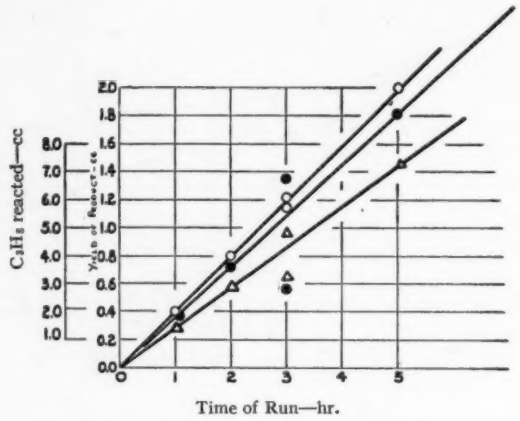

FIG. 3. Effect of length of run on reaction.
○ = CH_4, ● = H_2, △ = C_3H_8.

hydrocarbons with more than four carbon atoms per molecule. The previous work of Steacie and Dewar[4] has shown that these hydrocarbons consist principally of hexanes. (*b*) Decrease in pressure causes a marked decrease in the rate of disappearance of propane; this effect holds even when the rate is corrected for decreased quenching at low pressures. (*c*) The production of methane and hydrocarbons containing two and four carbon atoms per molecule increases with decreasing propane pressure. (*d*) The addition of hydrogen markedly alters the nature and the rate of the reaction. This effect becomes increasingly important with decreasing propane pressure. (*e*) The production of methane is much less prevalent with propane than with ethane at similar pressures.

Steacie and Dewar[4] proposed the following series of reactions to explain the products of the reaction of propane with $Hg(^3P_1)$ atoms:

$$C_3H_8+Hg(^3P_1)\rightarrow C_3H_7+H+Hg(^1S_0), \quad (1)$$

$$H+C_3H_8\rightarrow C_3H_7+H_2, \quad (2)$$

$$H_2+Hg(^3P_1)\rightarrow 2H+Hg(^1S_0), \quad (3)$$

$$2C_3H_7\rightarrow C_6H_{14}, \quad (4)$$

$$2H+M\rightarrow H_2+M, \quad (5)$$

$$H+C_3H_7\rightarrow C_2H_5+CH_3, \quad (6)$$

$$H+C_2H_5\rightarrow 2CH_3, \quad (7)$$

$$C_2H_5+C_3H_8\rightarrow C_2H_6+C_3H_7, \quad (8)$$

$$H+CH_3+M\rightarrow CH_4+M, \quad (9)$$

$$2C_2H_5\rightarrow C_4H_{10}, \quad (10)$$

$$C_2H_5+C_3H_7\rightarrow C_5H_{12}, \quad (11)$$

$$CH_3+C_3H_8\rightarrow C_3H_7+CH_4, \quad (12)$$

which certainly accounts adequately for the products obtained at high pressures where the "atomic cracking" reactions (6) and (7) were of minor importance. It is of interest to examine the above series more closely and to find out how well it fits the results obtained in the present investigation at low pressures.

On the basis of the above mechanism we can account for the pressure dependence of the rate corrected for quenching only by an increase in the rates of reactions (5) and (6) with decreasing pressure; this presupposes that hydrogen atoms recombine more readily on the wall than with another molecule as third body.

It has been found that the volume of methane produced per volume of propane reacted varies inversely as the working pressure of propane. This result is in reasonable agreement with the kinetics as outlined in the above mechanism scheme, since decreasing the working pressure of propane will lead to an increase in the rate of reaction (6) relative to that of (2).

The fact that the rate of production of methane is independent of the duration of the run within the limits covered may be taken as evidence that the stationary concentrations of C_3H_7 and H atoms are established instantaneously and that the initial [H] is not greatly affected by the accumulation of hydrogen in the system although eventually increased quenching by the accumulated hydrogen would increase the rate of production of H atoms, especially in runs at low propane pressures.

The question now arises as to the relation between the concentrations of propyl radicals, hydrogen atoms, and propane that are necessary to account for the increased rate of production of methane per volume of propane decomposed, bearing in mind the activation energies of reactions (2) and (6). The activation energy of reaction (2) has been estimated[12] to be 10 ± 2 kcal., and the assumptions[12] are that reaction (6) has an activation energy of $\leqslant 5$ kcal. For the rates of (2) and (6) to be equal at room temperature it would be necessary that the concentration of

propyl radicals be 3.35×10^{-4} times that of propane, or that the partial pressure of propyl radicals be 10^{-3} mm in the run at 3.0 mm. Since it is probable that propyl radicals recombine with about zero activation energy it is likely that the actual concentration of propyl radicals would be much lower than this figure. However, if "atom cracking" reactions be regarded as proceeding through the following steps:

$$H+C_3H_7\rightarrow C_3H_8^*, \qquad (6a)$$

$$C_3H_8^*\rightarrow C_2H_5+CH_3, \qquad (6b)$$

it would seem likely that they would proceed without real activation energy since (6a) is of the same type as the radical recombination reactions which probably do not require real activation energy.[15] If we then assume that $E_6=0$, we find that the rates of reactions (2) and (6) will be equal at room temperature when the concentration of propyl radicals is $10^{-3}\times[C_3H_8]$, a figure which seems much more likely.

Hence the above mechanism does offer an adequate explanation for the results obtained and indicates that the reactions of propane and ethane with $Hg(^3P_1)$ atoms are of the same type. The difference in the extent of atomic cracking with ethane and propane is, however, surprisingly large and, if we accept the value of 7 kcal. for the activation energy of the reaction

$$H+C_2H_6\rightarrow C_2H_5+H_2, \qquad (13a)$$

and assign zero activation energy to the reaction

$$H+C_2H_5\rightarrow 2CH_3, \qquad (13b)$$

we find that the above type of mechanism would indicate that atomic cracking, and hence methane production, would be much more serious with propane than with ethane, which is contrary to experimental fact. This discrepancy could be eliminated if either the activation energy of reaction (13a) were greater than 10 kcal. or if reaction (6), although occurring with zero activation energy, had a much smaller steric factor than (13b)—either because of spatial considerations or of more efficient deactivation of $C_3H_8^*$ than of $C_2H_6^*$. There has been considerable discussion about the activation energy of reaction (13a) which has been extensively investigated by the Wood-Bonhoeffer technique. However, it has been found that ethane reacts much more rapidly than does propane or butane with H atoms under those conditions, and it seems certain that the activation energy of reaction (13a) is smaller, or at least not greater than that of reaction (2). The assignment of a steric factor to reaction (6) small enough to account for the observed results would seem unwarranted on the basis of present information. The possibility of stabilization of $C_3H_8^*$ formed in reaction (6a) must be ruled out as a possibility since Steacie and Parlee[12] found that the residual propane was entirely light in their investigation of the reaction of deuterium atoms with propane. This also eliminates the possibility that reaction (2) is

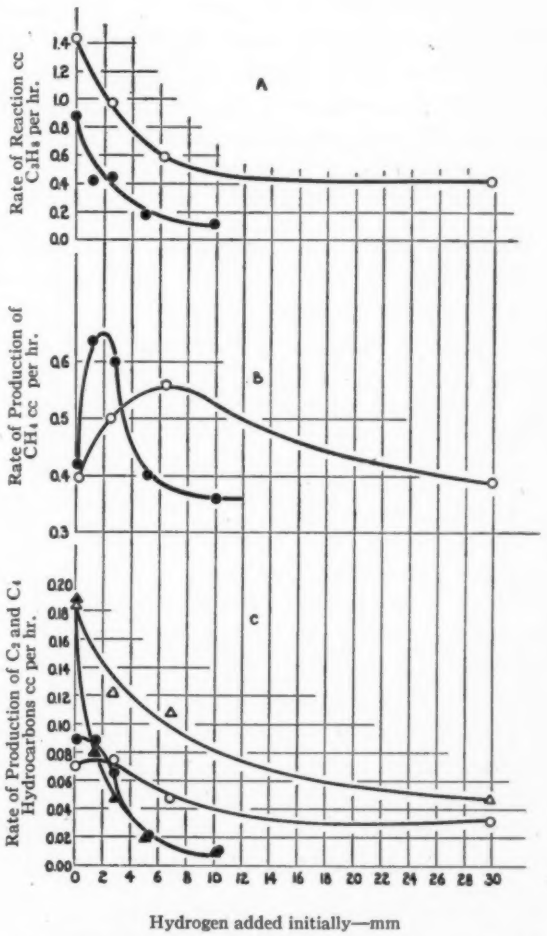
Rate of Reaction cc C3H8 per hr.
A
Rate of Production of CH4 cc per hr.
B
Rate of Production of C2 and C4 Hydrocarbons cc per hr.
C
Hydrogen added initially—mm

FIG. 4. Effect of added hydrogen on the reaction. Open points = runs at 3 mm; closed points = runs at 0.75 mm. In graph C, circles represent C_2 hydrocarbons and triangles C_4 hydrocarbons.

[15] E. Gorin, W. Kauzmann, J. Walter, and H. Eyring, J. Chem. Phys. **7**, 633 (1939).

faster than indicated but appears to be slow because of recombination of C_3H_7 and H. Although it is generally accepted that the activation energy of reaction (13a) is less than that of (2) the relative extents of exchange with ethane and propane are still somewhat uncertain; this point is now under investigation.

If we examine the steps leading to reaction between a paraffin hydrocarbon, $R \cdot CH_3$, and an active mercury atom more closely the first stage of the process could be represented by the formation of an "active complex" of the type:

$$R \cdot CH_3 + Hg(^3P_1) \rightarrow R \cdot CH_3 \cdot Hg^*. \quad (14)$$

This complex can now either react, and the most probable path would seem to be [7,8]

$$R \cdot CH_3 \cdot Hg^* \rightarrow R \cdot CH_2 + HgH, \quad (15)$$

or return to the original state. If the latter occurs, in a system in which the $Hg(^3P_1)$ atoms are fully quenched, the energy of the $^3P_1$ atom will be transferred to the paraffin molecule:

$$R \cdot CH_3 \cdot Hg^* \rightarrow R \cdot CH_3^* + Hg(^1S_0). \quad (16)$$

We have omitted the possibility of quenching to the metastable $^3P_0$ state since $Hg(^3P_0)$ atoms are known to be efficient in causing reactions due to atomic hydrogen in mixtures containing hydrogen molecules,[16] and, presumably, would also be efficient in their reaction with hydrocarbons.

The portion of the molecules that react by a C—H split (i.e., reaction (5)) could be expected to follow along the course outlined in the original mechanism. The excited molecule produced in reaction (16) may either react or be deactivated. Since it is possible that these molecules are similar to thermally activated molecules, we would expect them to decompose by a C—C split.[17–19] Since the extent of deactivation varies as the reciprocal of the total pressure we would expect that the rate of production of methane would also be a linear function of $1/p$—as found in the present investigation. The probable occurrence of ethylene in our products and the low quantum yield at high pressures strengthen the possibility of decomposition at low pressures and deactivation at high pressures of an active propane molecule.

The relative rates of reactions (15) and (16) will depend on the relative ease with which the C—H bond in question is broken to form the radical and HgH. It seems likely that the secondary C—H bonds in propane and butane, and the tertiary bond in isobutane would break more easily than would the primary bonds of ethane. Hence we would expect a relatively greater extent of C—H split with propane and the butanes than with ethane. Moreover it is likely that the active molecules formed in reaction (16) from propane and the butanes, because of the larger number of vibrational degrees of freedom in those molecules, would be longer lived than $C_2H_6^*$ and would thus have greater chances of deactivation. Therefore we would expect less C—C split to occur with propane and butane than with ethane at the same pressures. Hence the active molecule mechanism offers a reasonable explanation for the increased production of methane from ethane and propane with decreasing pressure of the hydrocarbon as well as for the difference found between ethane on one hand and propane and the butanes on the other. This mechanism would also indicate that the reaction of the paraffins with $Hg(^3P_1)$ atoms is of the same general type as the similar reactions of the olefins and diolefins since Le Roy and Steacie and Gunning and Steacie have shown that ethylene[20] and butadiene[21] both react, at least partially, by an active molecule mechanism. The fact that the rate varies inversely as $1/p$ (Fig. 1) is not in accord with the occurrence of an active molecule unless deactivation of $C_3H_8^*$ or recombination of atoms is faster at the wall than in the presence of another molecule as third body.

The explanation of the difference observed in the nature of the products obtained from propane with $Hg(^3P_1)$ and $Cd(^3P_1)$ atoms is also ambiguous. It seems certain that CdH is formed in

[16] E. Meyer, Zeits. f. Physik **37**, 639 (1926).
[17] R. N. Pease, J. Am. Chem. Soc. **50**, 1779 (1928).
[18] F. E. Frey and D. F. Smith, Ind. Eng. Chem. **20**, 948 (1928).
[19] E. W. R. Steacie and I. E. Puddington, Can. J. Research **B16**, 411 (1938).
[20] D. J. Le Roy and E. W. R. Steacie, J. Chem. Phys. **9**, 829 (1941).
[21] H. E. Gunning and E. W. R. Steacie, J. Chem. Phys. **12**, 484 (1944).

these reactions though the formation of HgH in the similar reaction is uncertain. Steacie, Le Roy, and Potvin[10] have pointed out the possibility that the difference between the $Cd(^3P_1)$ and $Hg(^3P_1)$ reaction of propane lies in the longer life of CdH which may therefore enter into reactions such as:

$$CdH+C_3H_8\rightarrow C_2H_5+CH_4+Cd(^1S_0).$$

However, if the reactions of the paraffins with $Hg(^3P_1)$ and $Cd(^3P_1)$ atoms proceed in both cases by an active molecule mechanism, then the energy distribution may be sufficiently different to account for the altered nature of the products with cadmium.

There is no clear-cut evidence available to help in deciding whether these reactions proceed entirely by a C—H split as originally proposed or by a combination of C—H split and the formation of an activated molecule as suggested in this paper. The activated molecule mechanism has the advantage that it allows explanation for the difference between the products obtained from ethane and $Hg(^3P_1)$ atoms and from the similar reactions of propane and the butanes with which the original mechanism cannot be reconciled unless drastic, and unwarranted, changes are made in the accepted value for the activation energy of the reaction between hydrogen atoms and ethane.

Experiments in the Presence of Added Hydrogen

The experiments carried out in the presence of added hydrogen establish the following: (*a*) The rate of propane disappearance decreases as the amount of hydrogen added initially is increased at constant propane pressure. (*b*) The rate of production of methane increases to a maximum and then decreases attaining a constant value when larger amounts of hydrogen are added. The yield of methane per cc of propane decomposed is increased by the addition of hydrogen; the extent of this increase is diminished by increase in the propane pressure. (*c*) The rate of production of C_2 and C_4 hydrocarbons is decreased by the addition of hydrogen; the extent of this decrease varies inversely as the working pressure of propane.

The experiments described were carried out with propane at 0.75- and 3.25-mm working pressure. It was found that in all cases the effect of added hydrogen was more pronounced in the runs at low propane pressure. Since propane quenches only slightly at these pressures we would have expected that the addition of a small amount of hydrogen, which quenches strongly, would have increased the concentration of H atoms and so increase the rate of both reactions (2) and (6). We find, however, that the rate of disappearance of propane is strongly retarded; the rate of (6) is increased with small amounts of hydrogen but is repressed by the addition of larger amounts. The addition of small amounts of hydrogen increases the rate of production of H atoms since the extent of quenching is greater than with propane alone. Increasing the rate of production of H atoms must increase somewhat the rate of production of propyl radicals by reaction (2). Since we assume that propane disappears only by the production of propyl radicals and since these radicals are produced principally by reactions (1) and (2), we must assume, to account for the decreased reaction rate, that reaction (1) is repressed to a greater extent than (2) is increased by the addition of hydrogen. This appears to be a reasonable assumption since the added hydrogen competes with propane for the available $Hg(^3P_1)$ atoms and since hydrogen atoms probably disappear more rapidly by reactions (5) and (6) than by (2). The increased rate of production of methane with small amounts of hydrogen is then due to an increase in the rate of reaction (6) which more than compensates for the decreased rate of the over-all production of propyl radicals in (1) and (2). The addition of larger amounts of hydrogen, beyond the pressure required for complete quenching, does not serve to increase the rate of production of H atoms but does increase the concentration of third bodies and so lowers the stationary H atom concentration by reaction (5), thus causing a decrease in the rates of reactions (2) and (6).

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Molecular Constants and Chemical Theories

V. Some Remarks on Physical Constants and Theories of Higher Valence States

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In answer to a recent article of Dr. Wheland, criticizing the previous papers of this series, some points of theoretical and experimental evidence are discussed. The criticism of the above paper is rejected in full (with the exception of a minor point on the calculation of ionic percentage contributions from bond moments). This article goes slightly beyond the previous ones in a number of points. Attention may be drawn to two of them. The question why different values of molecular constants are produced by the process of sharing or by a change of valency is discussed in greater detail. Furthermore, while maintaining that individual constants cannot distinguish between different structures or theories, it is shown that they can do so in conjunction. Indeed in conjunction they offer definite experimental evidence which supports the classical concepts but is not compatible with the semipolar double bond and its translation into resonance structures.

INTRODUCTION

IN a recent article[1] Dr. Wheland has brought forward some arguments against a series of articles[2] published by the present author and dealing with the relation of additive molecular constants with current theories of co-valency. The main arguments of Dr. Wheland are as follows:

He says that our calculations of the new additive bond moments are sometimes incorrect; that the latter do not lead to the experimental value of trimethyl amine oxide; and that the translation of coordinate bonds into resonance structures would also lead to some kind of additivity of physical constants.

We intend to show, first, that his calculation of the moment of trimethyl amine oxide is based on a tetrahedral structure which most certainly is not proved and most likely not the true one; secondly, that the results of our calculations are correct within the experimental error, and in this connection we shall have to say something about the meaning of the term "additivity" as far as such constants are concerned (Section A). Later we shall also show, thirdly, that these resonance structures do not permit any additivity except by fortuitous coincidence (Section B).

He then turns to wave mechanics and intends to show, that "the octet rule" (i.e., the theory of the semipolar bond) "is not an added arbitrary assumption but is a necessary consequence of quantum mechanics." Besides some objections against our interpretation of the theory of molecular orbitals, he intends to prove, in particular, that the three additional unpaired electrons of the excited NO radical cannot be localized at the N atom.

We intend to show, first, that wave mechanics in its present state of development cannot prove or establish at all the character of bonds in a complicated polyatomic molecule; secondly, that the particular proof of Dr. Wheland is based on the number of p-orbitals of a diatomic molecule and irrelevant for a polyatomic molecule (Section C).

Dr. Wheland also cannot understand why the process of sharing should produce a change in such a molecular constant like a bond moment. This is an experimental fact for all such constants and we shall show that it again is a very simple consequence of the same increase in the number of unexcited p-orbitals in the transition from the di- to the polyatomic molecule (Section C).

We take further exception to two more points in Dr. Wheland's article. The first is that in his restatement of the accepted principles of the theory of resonance—which otherwise is quite complete—he does not discuss in detail

[1] G. W. Wheland, J. Chem. Phys. **13**, 239 (1945).
[2] R. Samuel, J. Chem. Phys. **12**, 167, 180, 380, 521 (1944); quoted as Part I, II, III, and IV.

the energy differences between such resonating forms. But just this difference destroys additivity of molecular constants on the basis of this theory (Section B).

Furthermore, Dr. Wheland states that ionization potentials or molecular constants like dipole moments, etc. cannot distinguish between different theories. That is exactly the point of view which has been advanced in the previous articles of this series. It was shown that for this very reason no experimental evidence is available to establish the existence of the semipolar double bond or of the octet rule. However, although this is true as far as an individual constant of an individual molecule is concerned, we shall show nevertheless that several such constants in conjunction can distinguish and do distinguish between several possible structures and theories. Indeed, we will show that we possess today definite experimental evidence against the theory of the coordinate bond and/or its translation into resonance structures (Section D).

Finally, Dr. Wheland discusses our estimates of ionic contributions. It will be seen that he is partly correct in this particular criticism. But it will also be shown that this leaves us without any such methods, as all of them are equally unacceptable (Section E).

Again, as explained previously, we are here concerned only with molecules of Werner's first order, formed by a marked central atom.[3]

A

In the preceding papers[2] we have shown that additivity of molecular constants obtains on the basis of classical structures. The constants already analyzed in detail are the parachor or molecular volume, refractivities and bond moments. For all of them additivity is reached if different constants are introduced for different states of valency. In the meantime Burawoy[4] has made it clear that dative bonds or resonance structures are not necessary for the understanding of bond distances and the same could be proved for bond energies too.

Before discussing details of Dr. Wheland's criticism, it is, however, necessary to define more clearly what we understand when using the term "additivity."

We do not expect rigorous additivity of such constants, but additivity in first approximation only. The main reason has been pointed out by Fajans[5] two and a half decades ago, and we believed indeed that this is the generally accepted view, which did not need discussion. This reason why rigorous additivity does not exist is simply that we cannot neglect the attractive and repulsive forces between those atoms *not* linked together by chemical bonds. Thus in the most favorable possible case, the isomers of hydrocarbons, the energy of combustion, and therefore, the atomic energy of dissociation varies quite appreciably. For instance, for butane the difference between normal and iso-forms is 2.3 kcal./mole according to the latest figures.[6] That of isobutane is higher, simply because one hydrogen atom (positive end of a small dipole) approaches closer to a carbon atom (negative end of a small dipole) with which it is not linked, but by which it is attracted. In general the frequent variations of the valence angles are a good indicator of these forces. It is easy to see what much greater influence they will exert upon the additivity of our constants in less favorable cases such as the amines, which—as shown by their moments—change from the pyramid of the aliphatic to the planar structure of triphenylamine

As far as dipole moments are concerned, rigorous additivity is further prevented by the induction of one moment upon the others and by the solvent effect, both specifically mentioned in Part II. Thus, such a basic value as the moment of the nitro-group varies from 3.7 in nitro-methane (solution) to 4.8 in nitrobenzene (gas) and 4.5 (solution). We have started with

[3] We wish to protest at the outset against the terminology of "modern" as opposed to classical theories. Firstly, it is incorrect, as there never has been an unanimous acceptance of the semipolar double bond and its translation into resonance forms. For many people and at many places the classical are actually the modern structures. Secondly, such a terminology is bound to introduce into chemistry an emotional argument, which must not be permitted. To imply that a certain theory is more fashionable at a certain set of space-time coordinates would not increase its intrinsic value. We shall speak of "classical" and "resonance" theories, as before.

[4] Trans. Faraday Soc. **40**, 537, 1944; Chem. and Ind. (London), p. 434 (1944).

[5] Zeits. f. physik. Chemie **99**, 395 (1921).

[6] H. Pines, B. Kretinskas, L. S. Kassel, and V. N. Ipatieff, J. Am. Chem. Soc. **67**, 631 (1945).

a mean of 4.0 in order to account for the moments of both aliphatic and aromatic substances simultaneously. Also the valence angles are frequently not known. Thus for the angle ($Ph-N^{III}=N^{V}$) of azoxybenzene, we have taken that between double and single bond at N^{III} of 120° of the azides (this being the most natural assumption). But in NOCl the same angle is 116° and both measurements are within an experimental error of several degrees. It would be very easy to obtain almost strict additivity by means of a few changes of parameter within the experimental error, but it would be futile to aim at such rigorous additivity.

As no excessive accuracy of arithmetic calculation can overcome our lack of exact experimental knowledge, we have for that reason presented in Part III a survey of existing data only and have considered only the first decimal figure as significant. All calculations have been carried out on that basis. This paper (Part III) was marked as a first attempt quite clearly among others by the following sentences quoted from it (p. 327): "Mostly they (the new bond moments) represent values taken from one particular molecule and measurement, and are still unnecessarily afflicted by fortuitous errors. They could be improved by taking the average of several observations of a number of similar molecules. However, this method of direct comparison without taking means appeared better suited for the present purpose; namely, to demonstrate the existence of constant and additive bond moments according to the state of valency."

We do not believe that any higher accuracy of arithmetic calculation possesses any physical meaning—at least until more values are measured in the gaseous phase. However, if Dr. Wheland does not share this view and wants to go beyond such a first survey, he cannot logically use our new bond moments. He has then to do the whole calculation all over again from the very beginning. His bond moments then will vary from ours slightly, but will show the same additivity. Even so, he calculates for the β-form of the N-methyl ether of the nitrobenzophenone 1.7D as compared with our 1.4D and the observed 1.2D. That looks as if the error has been increased from about 15 percent to about 40 percent. But for the α-form, which fortunately exhibits the higher absolute values, the three figures are 6.0, 6.4, and 6.6D. Here the percentage error would increase from 3 percent to only 9 percent, which is an excellent agreement under the conditions stated above. This example, however, shows that it is not a question of percentage error at all, but of a small absolute error common to both. As the calculation results in too high values for one form and too low ones for the other, apparently the valence angles are not exactly those which we have assumed on theoretical grounds, thus producing the same absolute and small error in both cases but in opposite directions. For the reasons given above, we prefer a rough calculation like that and do not follow the temptation to reach a surprisingly accurate result by the introduction of a few special assumptions.

But as matters stand, any attempt to weaken our argument by criticizing small discrepancies, —even should they exist—is entirely irrelevant. The significant aspect of this controversy is that we have shown in Part III that first-approximation additivity exists, while on the basis of the theory represented by Dr. Wheland all such attempts have failed and have been given up.

Some details of Dr. Wheland's criticism are as follows:

(*a*) Dr. Wheland calculates a moment for the trimethylamine oxide from tetrahedral angles. He overlooks that the tetrahedral model has only been *assumed* by Sutton (Trans. Faraday Soc. **35**, 495 (1939)) in order to make an analysis of the complex diffraction pattern of this molecule at all possible. (As a matter of fact, a reinvestigation in Pasadena is not in good agreement with his results; private communication of Dr. Shoemaker.) At this time no such calculation has much meaning.

We have not ignored this molecule but have discussed it together with others of the same type, because only in this way is progress possible. The tetrahedral structure is already suspect because it would make this molecule the only one known with an abnormal N—O distance. We repeat that the decrease of the moment from R_3NO to R_3PO, *together* with the increase from R_3PO to R_3PS and to R_3PSe is incompatible in *any* theory with any of the geometrical structures yet suggested, while the moments of the related molecules R_3AsR_2', etc. indicate a frequent change of the structure for different R and R′, sometimes for the same molecule in different solvents. It is not unlikely that some have pyramidal structure with N or P at the apex, among them the amine oxide. We repeat that any such calculation is premature.

(*b*) There is indeed a misprint in the vector diagram of the nitrobenzenophenone oxime N-methylether. The

angle (N=C—C) has been given as 132°, while 122° has been used for calculation. We are, of course, sorry to have overlooked the mistake of the draftsman. Fortunately, the angle between double and single bond at the C atom is well known, and 132° is so unusual that it would lead to 96° for the (C—C—C) angle, so that the misprint is rather obvious. One inaccuracy occurs in the calculation of the *p*-nitrobenzophenone α-oxime N-methyl ether. At one time the author was experimenting with different bond moments for aliphatic and aromatic carbon; finally, however, it was decided that the inaccuracy of the experimental data does not yet warrant such a distinction at this time and a value of ~1.0 (clearly marked by the sign of inaccuracy) has been adopted by the N^{V}—C bond. However, a value of 0.8 was inadvertently not corrected in this one case. The final result is affected by about 0.1. The value for the azide group has been directly calculated from the *experimental* data of Sidgwick, etc., for which reference is given in Part II, not from his final theoretical value. Here for the nitrogen-carbon bond the value of Smyth rather than that of Sutton has been used. The latter includes the particular inductive and mesomeric effect of the aromatic ring. In the azides we find a radical, apparently acting as a unit and as such positive with regard to the ring, while the atom directly linked to the ring is negative with respect to it. It is difficult to predict what these two effects will be in such a case. If we use Sutton's value, the moment of the azide radicals comes to about .4 and three bond moments have to be radjusted by about .5. (The additivity of the moments of course remains.) This question belongs to those of detailed investigation which must be left open in such a first attempt, but we believe the present treatment to be the safer one until more data and also those of the gaseous phase are available.

Strict additivity will never be obtained and indeed has not been obtained for the bond moments of lower valency, generally accepted for a long time. Any one of a number of examples offered in Part III (for instance, the reconstruction of the two moments of the two forms of thianthrene sulphoxide on purely geometrical grounds) will convince anyone, who is conversant with this field, of the existence of additive moments of higher valence states.

We must repeat, therefore, that the additivity obtained for molecular constants on the basis of classical formulae is excellent. Even if the former could not distinguish between different types of covalent linkages, this in itself would remove the necessity for postulating the existence of a second variety of covalent linkage. It will be remembered how the parachor has been used as decisive argument for the existence of the semipolar double bond in numerous molecules. Carbon monoxide after all does not need a semipolar double bond because its electric moment is small, or the nitro group because its moment is large. Raman frequencies, energies of reaction, etc., have been discussed in Part II. Chemical experiments disclose the existence of bonding forces, but in general not their physical nature.[7] After careful study of all arguments, in our considered opinion, *there is not a single piece of experimental evidence left which could be used to establish the existence of a semipolar double bond*, or in fact, of any second variety of covalent linkage among non-aromatic first-order molecules, i.e., those formed by a central atom.

B

The existence of additivity of molecular constants does, however, more than to remove the experimental basis of the coordinate link and its translation into resonating structures. The latter are the only possible theoretical explanations of the dative link,[8] but they do not permit the existence of additivity at all. In order to show this, we have to discuss for a moment—like Dr. Wheland—the meaning of resonance structures.

We agree in general with his restatement of the theory of resonance, which indeed is part of our body of accepted knowledge. Strictly speaking every molecule resonates between all possible structures. But as the physical and chemical properties of the molecules show, most of them can be neglected for practical purposes, only a few are significant. This is just the point where the difference arises. The additivity of molecular constants has been shown to exist on the basis of classical structures. On the basis of coordinate structures such attempts to achieve additivity have failed (dipole moments) or have broken down (parachor). We therefore believe that the ground states of the molecules in question are represented by the classical formulae, and that the resonance structures of Dr. Wheland, although existing, are of negligible influence upon

[7] R. F. Hunter and R. Samuel, J. Chem. Soc. 1180 (1934); Chem. and Ind. **54**, 31, 467, 635 (1935); Nature **138**, 411 (1936); also reference 15.

[8] The original mechanism of Sidgwick is not admissible because the "lone pair" in most cases is the helium—like configuration s^2, which cannot produce chemical linkage. Cf. R. F. Hunter and R. Samuel, reference 7.

the unexcited state, because otherwise they would disturb this additivity.

One of the factors on which this influence of one structure upon the other depends is the energy difference between them (or the energy of excitation, if one of the structures is the lowest possible one). This energy is hardly ever discussed, and in order to obtain an idea of its order of magnitude, we turn to a concrete case where an estimate is possible. For instance carbon monoxide is represented as resonating between the three structures

$$C{=}O \quad (a); \quad C^+{-}O^- \quad (b); \quad C^-{\equiv}O^+ \quad (c).$$

The chemist indeed believed the molecule to exist in form (*c*) alone, or at most as a hybrid of (*a*) and (*c*). However, this would not explain the vanishing moment or the fact that its bond distance agrees with that of the classical structure (*a*) alone. Thus Pauling[9] introduced the additional form (*b*). We have shown earlier that (*b*) is chosen in such a way that it cancels (*c*) entirely, and (*a*), (*b*), and (*c*) together possess the properties of (*a*) alone; (*b*) plus (*c*) together have one-half of four bonds and no charge on either atom.

It is of course not possible to calculate the energy differences between such forms theoretically with any degree of certainty and we confine ourselves entirely to empirical figures. In other words, we construct a simple Franck-Condon diagram by means of the experimental values. The ground level C=O lies about 230 kcal./mole below the level of the separated atoms C+O. The ionization potential of C is 11.2 ev, the first electron affinity of O is 70.8 kcal./mole.[10] The level of the separated ions $C^+ + O^-$, therefore, lies 188 kcal./mole above the level of the separated atoms C+O. If the energy of the hypothetical semipolar double bond would even be 25 percent larger than that of the ordinary double bond (in reality it should be smaller according to the basic concept of the dative bond!), the level $C^+{-}O^-$ (*b*) would still lie 130 kcal./mole above the ground level C=O (*a*). For the (*c*) form the term difference becomes even larger on account of the higher ionization potential of O and the vastly negative (!) electron affinity of C. It is unlikely in the extreme that (*b*) and (*c*) could make the same contribution towards (*a*) as expected by Pauling in order to explain the electric moment and the bond distance.*

Now Dr. Wheland writes down a number of resonance structures, finds in them a formal similarity and concludes that "the nitrogen-oxygen bond is seen to be of more or less similar, but of course not identical type." Consequently he is not surprised that additivity exists. From a less formal, but energetical point of view it is, however, surprising indeed.

Let us consider only a few of his examples and write down their resonance structures; namely

Nitro-Group:

$$\underset{\text{50 percent}}{O^-{-}N^+{=}O} \quad ; \quad (1a) \qquad\qquad \underset{\text{50 percent}}{O{=}N^+{-}O^-} \quad , \quad (1b)$$

and *p-Nitrobenzophenone α-Oxime N-methylether*:

$$\underset{x \text{ percent}}{R_2C^-{-}N^+{=}O} \quad ; \quad (2a) \qquad\qquad \underset{y \text{ percent}}{R_2C{=}N^+{-}O^-} \quad . \quad (2b)$$

From the viewpoint of the resonance theory we would find the following conditions: In the nitro-group we have rigorous energetic degeneracy of the forms (1a) and (1b). Hence, the nitrogen-oxygen bond is a mixture of 50 percent $N^+{=}O$ and 50 percent $N^+{-}O^-$. In the oximes the moment of this bond has the same experimental value as in the nitro-group. Hence it must be again very nearly the same mixture, namely 50 percent of form (2a) and 50 percent of (2b). But these two forms are not energetically degenerated, and the molecule will be a mixture of *x* percent of (2a) and *y* percent of (2b). In the transition from (2a) to (2b) we replace a nitrogen-oxygen double bond by a nitrogen carbon double bond, the positive electron affinity of O by the vastly negative electron affinity of C, and so

[9] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1944), second edition.

[10] D. T. Vier and J. E. Mayer, J. Chem. Phys. **12**, 28 (1944).

**Note added in proof:* It has been suggested that the electrostatic attraction in $C^+{-}O^-$ would give 200 kcal./mole by itself. Such calculations on the basis of rigid ions have no meaning in a case like this, in which the two ions penetrate each other on account of the additional covalent bond and the two existing effects of deformation cannot be estimated.

forth. An estimate similar to that of carbon monoxide makes us expect an energy difference of at least 150 kcal./mole between (2a) and (2b), and x and y cannot be 50 percent each on energetical grounds. In order to make them so, the resonance theory has to assume that some other factor (for instance the unknown interaction integral which Dr. Wheland now expects to save the situation) differs from the same factor in the nitro group precisely to that extent which is necessary to make (2a) and (2b) of equal energy.* This is a fortuitous coincidence. But while the N-methylethers of these oximes share the nitrogen-oxygen bond with the nitro-group, the nitrates, etc., they also have the nitrogen-carbon bond in common with the diazo-group. This moment is the same for both. Hence—because (2a) and (2b) form a 50:50 mixture on account of the nitro-group—also the diazo-group must be a hybrid of 50 percent of the form (3a) and 50 percent of (3b). These two forms are:

$$R_2C^-—N^+=O \quad ; \quad (3a) \qquad\qquad R_2C=N^+—O^- \quad . \quad (3b)$$
$$\qquad\quad | \qquad\qquad\qquad\qquad\quad |$$
$$\qquad\quad R \qquad\qquad\qquad\qquad\quad R$$

One glance at their differences, namely the replacement of nitrogen-oxygen by nitrogen-carbon bonds and of the electron affinities, is sufficient to show that (3a) and (3b) cannot be energetically equal by themselves. Again some other factor has to operate fortuitiously to produce degeneracy and that 50:50 mixture necessary for additivity. This is a second coincidence, and quite unrelated to the first. And so it goes on. We can always proceed from one molecule to the next with which it has a bond and a bond moment in common. Hence we arrive at a surprising but logical conclusion. Because one of them, the nitro-group, is a hybrid of 50 percent each of two forms, *almost all of the very many molecules of higher valency and possessing similar resonance formulae, have to be such 50:50 mixtures of two forms within a very few percent.* Only then is additivity possible. On the basis of changing bond energies and stability this is not understandable at all, and the unknown factor has to readjust itself again and again to produce this entirely unforeseen energetic degeneracy.

* *Note added in proof:* In reality the exchange integral tends to make the difference between ground level and excited term still larger, not smaller.

In the moment we do not consider two or three molecules only, but a greater number, all interrelated by having one or the other bond and bond moment in common; these fortuitous coincidences become multiplied. It is not necessary to go into detailed discussion again. We have shown in Part IV to which lengths the resonance theory has to go to save the additivity of molecular constants. The point of disagreement is quite clear. We either accept this vast number of fortuitous coincidences on the basis of the resonance structures, or we do not accept them as coincidence, and the empirical fact of additivity of bond moments then forces us back to the classical structures as the essentially correct descriptions of these molecules in their normal states.

Furthermore, the same is true and even clearer for an additive molecular constant in which the contributions are not made by the bonds but by the atoms, for instance molecular refractivities or the molecular volume in terms of the parachor (cf. Part I). Sugden's way of calculating parachors by means of a *constant* value for the semipolar double bond is not possible any longer. We now have to replace it by calculations either on classical basis or on that of resonance structures. We take at random the first new value in Part I, that of double bonded oxygen [P](O=)=36.4. With this value the volume of a very great number of molecules may be calculated very correctly, using classical formulae, among them nitroso compounds or nitrites, where it is linked to nitrogen. With the same value we are able to calculate correctly the volume for instance of the following molecules:

	[P] Observed	[P] Calculated
Nitrous oxide	81.1	81.1
Nitro ethane	171.2	169.6
Azoxybenzene	444.7	447.8

But while in the simpler molecules the value of 36.4 stands for the oxygen atom pure and simple, for these three the same value would represent three different mixtures of (O=) and (O^-—). Similarly the basic value of 28.0 represents the double bonded C atom in all organic molecules. But according to the resonance theory, the same additive value sometimes stands for a mixture with C^+ or C^- or both. And the same is true of

many more atoms. Each case constitutes an unexplainable fortuitous coincidence.

As long as the semipolar double bond was thought to be a special mechanism, in which only one of the two atoms furnishes the binding pair of electrons, we wrote $N \equiv N \rightarrow O$, $O{=}N \rightarrow O$, etc., associated a definite value of the molecular constant in question with the coordinate bond and its symbol, and additivity of the constant could be achieved.

This position has become untenable; the semipolar double bond has to be translated into resonance with different percentages of ionic parent structures according to their varying energies of excitation. Apparently it has not been sufficiently realized that simultaneously the additivity of molecular constants has ceased. But this additivity nevertheless is an experimental fact and can be achieved on the basis of classical structures. Therefore, the additive molecular constants furnish direct experimental evidence against the existence of the semipolar double bond, or its translation into resonance structures.

C

We have taken the position that the theory of molecular orbitals does not constitute a theory of valency, but a theory of the electron configuration and term system of the completed molecule, which of course does not detract from its value. The reason is that in this theory the electrons are treated as independent and Heitler-London's energetical degeneracy due to electron exchange is absent. In order to reintroduce it a different assumption or postulate as to the counting of bonds is chosen.

This is possible because the conventional method, using the concept of bonding and antibonding electrons, also is based on an assumption or postulate and clearly, if such a postulate is necessary, it ought to be chosen in such a way that agreement is reached with the experimental facts. We have shown (Part II) that the conventional postulate leads to all kinds of difficulties and does not always agree with experimental facts. There is no need to discuss them here.[11]

[11] Dr. Wheland only offers an appeal to authority. We do not intend to follow him on these lines for reasons of principle. But we are entitled to request that such an appeal to authority should at least be made correctly. We left no doubt that this way of counting the bonds was introduced by Hund (Cf. reference 9 in Part II), and in his papers a full discussion may be found. Consequently it is not a question whether "Samuel's position is a tenable one," etc., but whether "Hund's position is a tenable one" and so forth. Surely this author has the same right as anyone else to interpret the Hund-Mulliken theory. His position, by the way, is by no means of recent date. We have added to it only the question whether the net effect of two electrons, paired but promoted, will be binding or not, and this without taking a definite stand.

Dr. Wheland makes quite a point about the terminology. He has overlooked that we have to choose another one, because we believe that the conventional terminology is misleading. This is so even in the two basic examples for which wave mechanical calculation has been carried through, and on which all generalizations are based, namely the hydrogen molecule and its ion. We find the supposedly bonding electron to produce no chemical bond but repulsion only in the excited terms of H_2^+, and the two supposedly anti-bonding electrons to produce a chemical bond in the term $(2p\sigma_u{}^2 - {}^1\Sigma)$ of H_2. This must be our excuse for not calling them bonding and anti-bonding but non-premoted and premoted electrons (with the same definition).

Dr. Wheland attempts to prove by means of wave mechanics that nitrogen cannot be pentacovalent, as the classical structures assume. How such a proof could be offered at the present time is difficult to see. It must not be forgotten —as it often is—that no rigorous wave mechanical calculation has been carried through for any molecule beyond the most simple ones. All our wave mechanical theories therefore are generalizations only, based on some plausible assumption. In fact, they are not theories but hypotheses. If proof was offered of an incompatibility of conventional wave mechanical theories with pentacovalency of nitrogen, first of all, an inquiry would be called for to find out which of the basic assumptions really causes the incompatibility, and whether this particular one really is as plausible as assumed. This point is of particular interest because the experimental evidence against the theory of the semipolar double bond is increasing, and—as will be seen presently—to our mind has already reached a point where it is decisive. The mere generalization of a theory, based on postulates and assumptions, of course, could not stand up against experimental evidence.

The easiest way to discuss these conditions

and differences of approach would be to write down in detail the electron configuration of such a polyatomic molecule. But to set up even an approximate function is a task involving great difficulties. We do not know how far we can trust the theory of molecular orbitals as a valence theory, and the pair bond theory needs higher approximations already for O_2. Therefore, we have not made actual use of the electron configuration of the diatomic molecule beyond showing the uncoupling of electrons previously forming a pair of the N atom, and as to its conversion into that of a polyatomic molecule, we did not yet intend to go beyond the remarks made previously in Part II (Section 2), which should be considered in conjunction with this chapter.

Of course, the electron configurations of polyatomic molecules suggested so far have not been derived by actual calculation and none can be considered as established or proved. They are more in the nature of generalizations worked out under certain assumptions, to make plausible certain characteristics of the molecule they intend to describe. The following remarks must be understood to be on a similar tentative basis only.

The most simple avenue of approach is one very much akin to Mulliken's[12] procedure, describing the electron configuration from "the point of view" of a particular atom. We consider for a moment the molecule in that extreme case in which it would be made up entirely of ions, which is also a fully legitimate approach. This procedure leads automatically to the completion of each quantum group before a new one is populated, and it also will always tell us whether a particular configuration is possible under the Pauli principle as it has to be applied to the polyatomic molecule.

We consider first a simple, non-controversial example. Thus the configuration of unexcited $CO(^1\Sigma)$, namely

$$\sigma^2(2s),\ \sigma^{*2}(2s),\ \pi^4(2p),\ \sigma^2(2p),$$

is nothing but the addition of the electron configurations of C^{2+} and O^{2-}. From $(C-s^2p^2)$ and $(O-s^2p^4)$ we obtain $(C^{2+}-s^2)$ and $(O^{2-}-s^2p^6)$. On approach, each being in the field of the other, the quantum number λ is introduced and if for once we write in geometrical rather than in energetical sequence and take into account the deformation of the ions,[13] we obtain:

$$[C^{2+}-\sigma^2(2s)]+[\pi^4(2p),\ \sigma^2(2p),\ \sigma^2(2s)-O^{2-}]$$

which on decrease of the internuclear distance becomes for the covalent molecule:

$$C^{II}-\sigma^2(2s),\ \pi^4(2p),\ \sigma^2(2p),\ \sigma^2(2s)-O^{II}.$$

The only difference is that in this geometric sequence we cannot say which of the two $\sigma^2(s)$ groups is premoted; but also in the first form we do not know to which atom the premoted group belongs. The two functions are entirely identical.

Applying the same method to nitromethane, we obtain for the approaching ions:

$$[R^- -\sigma^2(2s)]+[N^{5+}] \\ +2[\pi^4(2p),\ \sigma^2(2p),\ \sigma^2(2s)-O^{2-}].$$

In the covalent molecule we have three distinct axes of preference and therefore should have three λ-type quantum numbers, say u, v, and w. Each of these possesses three possible values for p-electrons ($l=1$) e.g., σ_v, $+\pi_v$, $-\pi_v$. Therefore, we should obtain at small internuclear distances for the covalent molecule formed by these ions:

$$\begin{array}{l} \qquad\qquad\qquad\qquad \pi_v^4(2p),\ \sigma_v^2(2p),\ \sigma_v^2(2s)\text{—O} \\ \text{R—}\sigma_u^2(2s)\text{—N} \\ \qquad\qquad\qquad\qquad \pi_w^4(2p),\ \sigma_w^2(2p),\ \sigma_w^2(2s)\text{—O.} \end{array}$$

Under the Pauli principle, we find places for 2×6 non-premoted p-electrons and as many again for premoted ones. The two O atoms contribute only 8 p-electrons and those of $N(sp^4)$ find places among the non-premoted ones, while its s-electron is accommodated under the quantum number of the third axis. The N-atom is now surrounded by four pairs of p-electrons and one pair of s-electrons. Of these 10 electrons 5 originally belonged to nitrogen. The exclusion principle has not been violated.

We have now to investigate in which way these 10 electrons form bonds. Incidentally, in

[12] R. S. Mulliken, (e.g.) Phys. Rev. **40**, 55 (1932).

[13] The chemical symbols stand for the cores including the K-shell.

the theory of molecular orbitals these 10 electrons would form 5 covalent bonds according to Hund's theorem, and they would be bonding ones "from the point of view" (Mulliken[12]) of the two O-atoms and of the radical R. However, we cannot accept this concept of individual bonding and antibonding electrons, which does not agree with the experimental facts.[14] But this hypothesis has been introduced for a very good reason. The method of molecular orbits only recognized the molecule as an entity and does not know of any distinctive groups in it. It can tell us the number of electrons in the molecule and their quantum numbers, but cannot identify them with the electrons of the separated atoms. Without a further hypothesis it therefore cannot make statements on the formation of the molecule or the mechanism of linkage. Thus by expressing *faute de mieux* a molecular orbital in terms of a linear combination of atomic-orbitals, in reality we reduce the quantum numbers u, v, and w of the molecule to those of the free atoms. Then, of course, any attempt to localize the electrons in the neighborhood of one or the other atom only expresses in different language London's original difficulty about the unpairing of the p-electrons of N and O. But the kinematic meaning of the quantum numbers (e.g., u, v, w) becomes less and less known the more complex the molecule and with it the description and designation of the electrons at small internuclear distance. It becomes less and less possible to predict whether the terms omitted in a simplified theory are not of importance, and these make the difference between an atomic and a true molecular orbital. In the diatomic molecule, l has already lost its significance, while λ is retained. In our tetra-atomic example it is plausible to assume a quantum number which is the projection of l upon the axis, but we cannot make any statement with any assurance about the relation of u, v, w to the λ of the original diatomic radical. Hence we do not know whether it is permissible to build up the wave function as a combination of two atomic orbitals only, as in the diatomic molecule. Hence, any localization of the electrons in a diatomic radical like NO cannot tell us anything about the localization in a molecule such as RNO_2. We would even go further. The theory of molecular orbitals in its conventional interpretation as a theory of valency leads to a hydrogen molecule which to 50 percent is formed by atoms, to 50 percent by ions H^+ and H^-, while CH_4 would be formed to 73 percent from ions (cf. Part II). It is well known that this stupendous disagreement with the experimental facts is directly due to the independence of the electrons, i.e., the absence of the Heitler-London effect. Hence the basic postulate of the conventional interpretation is not well chosen, and this theory gives an entirely incorrect description of the process of the formation of a covalent molecule. *It is this process which is fundamental for a theory of valency.* This is well known and generally acknowledged, and the mere fact that this method needs a further hypothesis such as the bonding and antibonding character of individual electrons again confirms its inability to make conclusive statements on the nature of the bonds, i.e., the localization of the electrons. It is, therefore, our view that the method of molecular orbitals gives us final and conclusive information about the terms system of a molecule, but no statement about its formation. Therefore, no statement about the number or nature of its bonds can be relied upon.

For such problems the pair bond theory is much more trustworthy. It would be the final arbiter if a real calculation of a higher polyatomic molecule could be carried through, but unfortunately this theory needs higher approximations already for a simple molecule like O_2. Nevertheless, it is quite interesting to consider just this case briefly.

In its unexcited state ($2s^2$, $2p^4 - {}^3P$) the O-atom possesses four p-electrons. Six different distributions of the four p-electrons over the three λ-values 1, 0, -1 are possible, namely $2+2+0$, $2+1+1$, $1+2+1$ and so forth. If we take any one of them alone, we have an oxygen atom which cannot be more than divalent, because no excitation increases the number of unpaired electrons beyond two. But a combination of two such atoms leads only to the diamagnetic oxygen molecule. The paramagnetic oxygen molecule of the pair bond theory essentially is obtained by the hybridization of all these

[14] Part II, p. 185 ff, cf. also the remark on $H_2H_2^+$ above.

possible distributions or terms. Thus each of the λ-groups of both the O-atoms alternatingly is occupied by a pair of *p*-electrons and by a single electron. Therefore, we obtain two unpaired electrons on the molecule. There is no reason why the latter should not produce an additional chemical linkage according to the basic concepts of the pair bond theory, and the discussion of the ozone molecule in the next section shows that they do. The pair bond theory does not tell us how they are localized at small internuclear distance in O_2 and O_3, but we get in ozone either one tetravalent or two trivalent O-atoms, both being definite violations of the Octet rule. This process, of course, is intimately connected with the fact that there are possibilities for six pairs of *p*-electrons in the diatomic, for nine pairs in the triatomic molecule. Only a molecule made up entirely of rare gas atoms would fill in all of these; every chemically known molecule will possess incompleted or unoccupied groups.

The same, of course, is true for the excited N atom in (sp^4). We have the same configuration of four *p*-electrons, and the hybridization over different distributions must lead again to the two unpaired electrons of a diatomic molecule, as in O_2. Only this time the single *s*-electron has to be added to the number of those electrons which in the pair bond theory represent free valencies.

These few remarks should be understood to be of provisional and tentative nature, until a more detailed treatment can be presented. They are made here only for the purpose of showing how dangerous it is to transfer results from the atom to the diatomic and from there to the polyatomic molecule. At the present state of its development, when even the calculation of a higher diatomic molecule is not possible, wave mechanics cannot give final answers to questions of the polyatomic molecule. This is particularly true if the orbital method is used for problems connected with the formation of the molecule, such as the localization of the electrons, i.e., the nature of the bonds. It appears that Dr. Wheland agrees with us on one important point, namely, that we now do not possess a single experimental fact which could establish the existence of a dative bond as a second variety of covalent linkage. If indeed wave mechanics is the only basis of this concept, then for the time being this basis is weak. And if we find one single experimental fact, such as the impossibility of additivity or the characteristics of the ozone molecule, which is not compatible with the theory of the dative bond, then we should attempt to change one of the many postulated hypotheses in the structure of the wave mechanical theory of the polyatomic molecule, without being unduly intimidated by them.

We now wish to turn briefly to the N_2O molecule in order to meet a further objection of Dr. Wheland. Using the same approach, we find for the electron structure of the approaching ions:

$$[O^{2-} - \sigma^2(2s), \sigma^2(2p), \pi^4(2p)] + [N^{5+}] + [\pi^4(2p), \sigma^2(2p), \sigma^2(2s) - N^{3-}].$$

Nitrous oxide is a linear molecule, but the two fields have opposite directions and should be treated as independent, because in general the electron will have different λ-values in each of them. We therefore obtain for the covalent molecule at small distances:

$$O^{II} - \sigma_u^2(2s), \sigma_u^2(2p), \pi_u^4(2p) - N^{V} - \pi_v^4(2p), \sigma_v(2p), \sigma_v^2(2s) - N^{III}.$$

We now compare this configuration with that of nitric oxide, which leads us to the question of why molecular constants change in the process of sharing or in different states of valency. In its ground state $^2\Pi$ (again written in geometrical sequence), the configuration of NO is

$$N - \sigma^2(2s), \pi^4(2p), \sigma^2(2p), \pi^*(2p), \sigma^2(2s) - O.$$

Here altogether 11 electrons are in the combined field of N and O. The above configuration of a polyatomic molecule clearly shows that in a nitroso compound R—N=O one of these electrons, namely the odd $\pi^*(2p)$ electron, essentially will be in the combined field of N and C, and only 10 electrons will essentially remain in that of N and O. And in nitrous oxide three electrons, namely $\pi^*(2p)$ and (after excitation to sp) the $\sigma^2(2s)$ group nearest to N^V, essentially are transferred to the field between N^V and N^{III}, leaving only 8 electrons belonging essentially to the field between N^V and O. This is in perfect agreement with the physical properties

of the molecules. Its meaning is that the electron density between N and O is gradually reduced by the partial transfer of these electrons of N, the latter becoming more positive with respect to O, as discussed in Part II and III in detail. Hence the moment of the nitrogen-oxygen bond is 0.1D in nitric oxide, 2.0D in the nitroso stage, and 4.4D in the nitro-group and in nitrous oxide. A similar behavior of molecular refractivities has been known a long time. As refractivities measure the forces in inverse ratio with which the electrons are held by the atoms, the more positive the N atom becomes, the smaller its atomic refractivity:

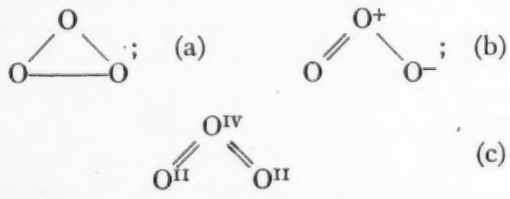
$$R[N^{III}]=3.90, \quad R[N^{V}]=2.52.$$

What we call the molecular volume is a function of the attractive and repulsive intermolecular potentials, in the main due to the outer electrons. Hence it follows closely this rearrangement of the electrons, as already discussed in Part I.

In this connection attention may be drawn to earlier considerations which indicated that in a covalent molecule A—B—C electron exchange occurs between B and both A and C, but not between A and C across the central atom.[15]

D

We now return for a moment to the experimental evidence. Because if Dr. Wheland was right, and the octet rule was rigorously valid in the second period, the ozone molecule could not exist. Indeed we have already pointed out that the properties of the ozone molecule constitute the direct experimental proof of our concept. The ozone molecule forms an isosceles triangle with an angle of 122° at the apex.[16] At the same time a dipole moment of 0.5D has been observed.[17] Of the possible structures left

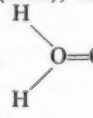


(a) would not possess an electric moment at all, while that of the two resonating forms of (b) would be many times larger. Only (c) with tetracovalent oxygen at the apex meets both conditions, and according to its bond moment, is a complete homologue of SO_2. As the ionization potential increases from Se to S and O (9.5, 10.3, 15.6 ev, respectively), so the bond moment decreases, and $\mu(O^{IV}=O^{II})$, calculated to slightly more than 0.5 from formula (c), fits excellently into the series of $\mu(S^{IV}=O)=1.6$ and $\mu(Se^{IV}=O)=2.1$. Of course, if tetracovalency is possible for $O(s^2p^4)$, then excited $N(sp^4)$, with the additional uncoupled s-electron, is pentacovalent. On the other hand, applying exactly the same argument of Dr. Wheland, it could be shown that form (c) is impossible and only form (b) could be the true one, which is entirely ruled out by the dipole moment.[18]

The existence and properties of the ozone molecule therefore establish a violation of the octet rule also for the atoms from Li to Ne. They show the configuration $2p^4$ to furnish 4 covalent bonds from the triatomic molecule onwards. Incidentally this is the third piece of direct experimental evidence against the concept of the semipolar double bond, furnished by additive molecular constants alone. It shows that in favorable cases these constants in combination finally possess the quality to decide between conflicting theories. The two other pieces of direct evidence are, first, that the additivity of molecular constants is better by far on the basis of classical than of semipolar structures (cf. Part I), and, secondly, that the translation of the latter into resonating structures prohibits additivity entirely, although the latter is an empirical fact.

It is of course fortunate that we can close even the theoretical argument on the high note of direct experimental evidence instead of abstract reasoning, due to the recent measurements mentioned above.[16,17] However, in reality the mere existence of the nitro-group or of N_2O_5

[15] H. Lessheim and R. Samuel, Proc. Ind. Acad. Sci. (Bangalore) **1**, 623 (1935); also Phil. Mag. **25**, 664 (1938).
[16] W. Stand and R. A. Spurr, J. Am. Chem. Soc. **65**, 179 (1943).
[17] C. P. Smyth and G. L. Lewis, J. Am. Chem. Soc. **61**, 3063 (1938).

[18] Geib and Harteck (Ber. **1551** (1932)) claim the isolation of a second form of peroxide, 

also with tetracovalent oxygen.

always appeared to be sufficient to decide the point of issue, because the conventional resonance structures formed by the N^+ ion are much too highly excited terms of these molecules. It has been clear a long time[7] that the four covalent bonds ascribed to N^+ cannot be furnished by an unexcited ion $N^+(2s^22p^2)$; only an excited ion $N^+(2s2p^3)$ can be discussed. Again the helium-like configuration has to be fissured before tetracovalency becomes effective exactly as in $C(2s^22p^2)$. Accordingly, we cannot consider the ionization energy of a p-electron of N (14.48 ev) but of its s-electron, which is about 90,000 cm^{-1} higher. Hence the level $(N^+(sp^3)+2O)$ lies about 580 kcal./mole above the level of the unexcited atoms (N+2O). The ground state of $\frac{1}{2}N_2O_5$ lies 230 and that of the nitro-group (taken from organic nitro-compounds) about 190 kcal./mole below the same level. We thus would obtain a minimum value of 320 to 380 kcal./mole for the adiabatic dissociation, i.e., the true bond energy, of the nitrogen-oxygen bond, which seems much too high, particularly when compared with the 121 of the dissociation energy of NO.

E

Finally we have to discuss the percentage contribution of ionic forms, and that is the one point in which we partly agree with Dr. Wheland. It is incorrect, as we did, to compare the shift of the electron pair with the whole bond distance. But it is also wrong to compare it with half of that distance, as Dr. Wheland suggests. If the bond in question would not possess any moment at all, the electrons would not be situated in the middle between the atoms, but so as to compensate the center of gravity of positive electricity. Thus in the bond, $S^{VI}{=}O$, the two pairs are in the field of S^{6+} and O^{2+}. Without going into the details of screening effects, etc., it can be seen that the electrons must be much closer to S to obtain zero moment, and we obtain a factor larger than $\frac{1}{2}$. In general this method will give lower percentages of ionic character than Pauling's. Hence the two methods will disagree.

In fact, we do not possess any method at present which would permit us to estimate the percentage of ionic contribution. Without going into details, we have mentioned in Part II that Pauling's second method[9] also is not easily acceptable because it uses the additivity of bond energies as a criterion. After having discussed the meaning of additivity in Section A of this article, we are able to express our objections more clearly: The deviations from rigorous additivity which are used as the basis of these estimates may be due to the contributions of ionic forms. But they also may be due, and some part of them certainly are due, to the neglected secondary forces acting between atoms not linked by a chemical bond.

The energy difference between normal and isobutane mentioned above should make this already clear.

However, the hydrocarbons are the case which approaches most closely the ideal one. For an inorganic molecule we obtain a different picture. For instance, the mean of the dissociation energies of Cl_2 and I_2 is 46.3. D(ICl) is 49.4. That leaves us with a difference of 3.1. But if we would have taken as the strength of the bond I—Cl one-third of the dissociation energy of ICl_3, as is done so often in other cases, we obtain 41 ± 2,[19] and therefore a negative (!) resonance energy. The secondary effect of repulsion between the three Cl atoms (the negative ends of three moments) contributes much more than any possible resonance with ionic forms. But ICl and ICl_3 are almost the only case where we can make such a direct comparison, and for any other even slightly complicated molecule it becomes impossible to say how much of these energy differences is in reality due to the bond energies and how much to repulsive and to attractive secondary forces.

CONCLUSIONS

Controversies can arise in science only at a time when the experimental evidence is not yet sufficiently advanced to decide a particular question once for all. We have shown that no experimental evidence exists which necessitates to postulate a semipolar double bond in those molecules, with which these articles are concerned; that therefore on energetical grounds the corresponding ionic resonance forms may be neglected for all practical purposes; that wave-

[19] The uncertainty is due to the sublimation energy of ICl_3, which here is taken to be 8 kcal./mole, according to Forcrand's rule.

mechanical theories can be in agreement with a violation of the octet rule for nitrogen and oxygen, if applied to the polyatomic as distinct from the diatomic molecule; and finally that the experimental evidence as furnished by the additive molecular constants does not agree with the concept of a coordinate linkage in such molecules, but only agrees with the classical structures.

But we readily admit that this empirical evidence—although already decisive in our belief—is not yet overwhelming and is of recent date. At this time we therefore only ask for a re-examination of the basic concepts of the chemical theories of valency. Such a re-examination appears to be called for, and it should be undertaken without any preconceived ideas to which we have become accustomed, and starting at the very roots. It should be carried out from a point of view which has been expressed by Born[20] as follows:

"My advice to those who wish to learn the art of scientific prophecy is not to rely on abstract reason, but to decipher the secret language of Nature from Nature's documents, the facts of experience."

[20] M. Born, *Experiment and Theory in Physics* (Cambridge University Press, Cambridge, 1943).

Editor's Note:—The foregoing article has been resubmitted several times without significant alteration after several severe criticisms on essential points of logic and fact by referees of the Journal. Many of the opinions expressed in the article are not those of the editorial board of the *Journal of Chemical Physics*.

Chain Initiation in Catalyzed Polymerization

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SCHULZ[1,2] and Mark and Josefowitz[3] have shown that the polymerization rate of methyl methacrylate, styrene, vinyl acetate, and isoprene catalyzed by benzoyl peroxide, or of styrene catalyzed by tetraphenylsuccinonitrile, can be expressed by Eq. (1).

$$\frac{d(M)}{dt}=\text{constant}\times(C)^{\frac{1}{2}}(M)\left[\frac{K(M)}{1+K(M)}\right]^{\frac{1}{2}}, \quad (1)$$

where (M) = monomer concentration, (C) = catalyst concentration, and K = constant. This expression is not readily derived from the usual assumption that peroxide dissociates into free radicals which can initiate growth. To obtain Eq. (1), Schulz[1,2] assumes that the catalyst and monomer exist in equilibrium with a complex (equilibrium constant K in Eq. (1)) which rearranges to give the first radical unit in the growing chain. The equilibrium constants of Schulz indicate appreciable amounts of this complex, but no independent evidence for the complex exists. In most cases the values of K show the complex to be more stable at higher temperatures which is unexpected.

However, Eq. (1) may be derived without postulating a complex. The considerations applied by Franck and Rabinowitsch[4] to photolysis in solution appear to be applicable here. The essential idea is that two fragments from a dissociated molecule find themselves held in a cage of solvent molecules, and therefore the radical pair collide many times with each other and the surrounding molecules before they can diffuse apart. Thus, in benzene at room tem-

[1] G. V. Schulz and E. Husemann, Zeits. f. physik. Chemie **B39**, 246 (1938).
[2] G. V. Schulz and F. Blaschke, Zeits. f. physik. Chemie **B51**, 75 (1942).
[3] H. Mark and D. Josefowitz, Ph.D. Thesis of D. Josefowitz at Brooklyn Polytechnic Institute (1945).
[4] J. Franck and E. Rabinowitsch, Trans. Faraday Soc. **30**, 120 (1934).

perature a molecule may make about 10^{10} jumps per second from one equilibrium position to another but undergoes about 10^{13}–10^{14} collisions in the same time.[5] From this discussion it is expected that if two radicals or a radical plus a molecule are in contact with each other in solution and may react with a very low activation energy, then in general reaction occurs before the components can separate.

The mechanism below is similar to one proposed by Price[6] but with kinetics modified in view of above discussion. Here the peroxide is assumed to dissociate in a first-order reaction into two fragments (step (1)),

		Rate
(1)	$(\phi COO)_2 \xrightarrow{k_1} 2\phi COO-$	$k_1[(\phi COO)_2]$
(2)	$\phi COO- + \phi COO- \xrightarrow{k_2} (\phi COO)_2$	$k_2[\phi COO-]$
(3)	$\phi COO- + M \xrightarrow{k_3} P_1^-$	$k_3[\phi COO-][M]$
(4)	$P_r^- + M \xrightarrow{k_4} P_{r+1}^-$	$k_4[P_r^-][M]$
(5)	$P_r^- + P_n^- \xrightarrow{k_5}$ Inactive Polymer	$k_5[P_r^-][P_n^-]$

which either recombine (step (2)) or add to a neighboring monomer (step (3)) before they can diffuse apart. Only those radicals which come from the same catalyst molecule recombine (the "Primary Recombination" of Franck and Rabinowitsch), so the rate of recombination is first order. For step (3), however, the rate will depend on the number of radical pairs per unit volume and on the concentration of monomer in the solvent layer around each pair. After the addition of a monomer to a radical the free valence on the new radical is likely to be separated from the other peroxide fragment, which also proceeds to initiate polymerization. The isolated radicals, P_r^-, proceed in propagation (4) and termination (5) with the usual kinetic dependence.

The steady state procedure applied to this mechanism yields (2), which has the same form as (1).

$$\frac{d(M)}{dt} = \frac{k_4}{k_5^{\frac{1}{2}}}(C)^{\frac{1}{2}}(M)\left[\frac{k_1(k_3/k_2)(M)}{1+(k_3/k_2)(M)}\right]^{\frac{1}{2}}. \quad (2)$$

The factor $(k_3/k_2)(M)/[1+(k_3/k_2)(M)]$ is the fraction of radicals which initiate polymerization. The equilibrium constant K is now interpreted as the ratio of k_3 to k_2 and from the data of Schulz the fraction initiating can be calculated. That k_3/k_2 should increase with temperature is reasonable.

McClure, Robertson, and Cuthbertson[7] suggest that at 66°C the decomposition of benzoyl peroxide in benzene occurs about 75 percent by (2a).

$$2\phi COO- \xrightarrow{k_{2a}} CO_2 + \phi COO\phi. \quad (2a)$$

This will not change the form of Eq. (2) but for k_2 is substituted k_2+k_{2a}. Some of the other possible reactions do not affect the form of Eq. (2).

The mechanism outlined yields the polymerization rate equation of Schulz and Mark, agrees with first-order decomposition of benzoyl peroxide in benzene, and accounts for the higher decomposition rate in monomer in the fashion suggested by Price.[6]

I wish to thank Dr. Frank R. Mayo for helpful discussions. The kindness of Professor H. Mark in allowing me to read the unpublished work referred to is deeply appreciated.

[5] A. E. Stearn, E. M. Irish, and H. Eyring, J. Phys. Chem. **44**, 981 (1940) and E. A. Moelwyn-Hughes, *Kinetics of Reactions in Solution* (Clarendon Press, Oxford, 1933), p. 20, were used for equations and data for estimates.

[6] C. C. Price, Ann. N. Y. Acad. Sci. **44**, Art. 4, p. 351 (1943).

[7] J. H. McClure, R. E. Robertson, and A. C. Cuthbertson, Can. J. Research **20B**, 103 (1942).

Letter to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

High Velocity Fragments in Secondary Photochemical Processes

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Received November 13, 1945

MORE precise study of the vapor phase photolysis of hydrogen iodide by light of λ2537A (temperature range some 102°C to 190°C, partial pressure of hydrogen iodide some 200 mm Hg) has shown the inhibitory effect of iodine to be even slightly less than previously reported,[2] the rate constant ratio k_3/k_2 (*vide* infra) being 3.8±0.4 instead of 4.9. Current studies with Julius Roth have shown an appreciable enhancement of this iodine inhibition by addition of cyclohexane vapor, which is transparent to the light employed, and chemically indifferent to the other substances. That the additional retardation is not caused by *chemical* side reactions, as say $H+C_6H_{12}\rightarrow C_6H_{13}$, is indicated by the dependence of the effect on cyclohexane concentration. This is marked for small amounts (~30 mm Hg) but rapidly approaches a limiting value unaffected by further increase, even up to pressures as large as 2000 mm Hg. This functional relation is typical of quenching or deactivating processes. The results are in accord with the following expanded mechanism

$$\begin{aligned} HI+h\nu &\rightarrow H^*+I \\ H^*+HI &\rightarrow H_2+I \quad k_2 \\ H^*+I_2 &\rightarrow HI+I \quad k_3 \\ H^*+M &\rightarrow H+M \quad k_4 \\ H+HI &\rightarrow H_2+I \quad k_5 \\ H+I_2 &\rightarrow HI+I \quad k_6 \\ 2I+M &\rightarrow I_2+M \end{aligned}$$

The symbol H* refers to a hydrogen atom of abnormally high velocity, while H refers to one of "thermal" velocity distribution determined by the prevailing temperature. The symbol M for the deactivating molecule refers predominantly to cyclohexane in the present studies. The limiting ratio k_6/k_5, characteristic of "thermal" hydrogen atoms, has been found to be 7.0±0.4 at 155°C. The ratio k_3/k_2 =3.8±0.4 refers to abnormally fast hydrogen atoms, of energy deduced below.

The process

$$HI+h\nu_{2537}\rightarrow H(^2S_{\frac{1}{2}})+I'(^2P_{\frac{1}{2}})$$

is exothermic by some 20 kilocalories per mole. The mechanical condition of conservation of momentum requires this to appear almost entirely as kinetic energy of the hydrogen atom. The difference in the values of k_5 and k_6 is probably due in part to a difference in activation energies of the order of a few tenths of a kilocalorie per mole. This difference would of course be "leveled" by such a large kinetic energy. The ratio 3.8 would then appear to be more nearly representative of the ratio of *frequency factors* for k_6 and k_5.

Studies of the photoreaction of methyl iodide with hydrogen iodide, bromide, and chloride indicate a reaction mechanism formally similar to the above, the primary step being

$$CH_3I+h\nu\rightarrow CH_3{}^*+I'.$$

Current studies indicate that the effect of cyclohexane addition is to cause enhancement of iodine inhibition considerably greater than that in the hydrogen iodide photolysis. This may suggest that the activation energy differences in the secondary steps involving "thermal" methyl radicals are greater than in those involving hydrogen atoms.

[1] Present address, Clinton Laboratories, Knoxville, Tennessee.
[2] R. A. Ogg, Jr. and R. R. Williams, Jr., J. Chem. Phys. 11, 214 (1943).

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